

LEACHABILITY OF SOLID INDUSTRIAL WASTES



July, 1981

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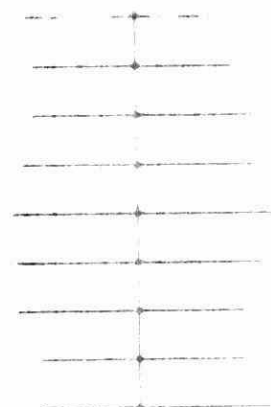


Ontario

Ministry
of the
Environment

The Honourable
Keith C. Norton, Q.C.,
Minister

Graham W. S. Scott, Q.C.,
Deputy Minister



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APPENDIX I

TEST MATERIALS

Sample No.	Laboratory No.	Description	Source
70	S1-26.1	Foundry sand	Walker Bros
71-75	S1-34.1-5	Waste	Cyaramid
76	S1-35.1	Oil treatment	Universal Pneumatics
77-81	S1-52.1-5	Lime waste	Sarnia
82-84	S1-54.1-3	Brass smelter	Sarnia
85	SE15-9001	Bag-house dust	Burlington s
86	S1-67-1	Bag-house dust	Atlas Steel
87-89	S1-44.1	Solidified steel waste	Atlas
90	SE17-9007	Spent catalyst	Texaco
91	S1-63.1	Calcium phosphate	Cyanamid

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<u>Sample No.</u>	<u>Laboratory No.</u>	<u>Description</u>	<u>Source</u>
1	S7-28.29	Settling pond	Borg Warner
2*	S7-31.129	Silver Smelter	Cobalt
3	S8-33.48	Buffing compound	Rockwell
4	S8-41.6	"Old" fly ash	Ontario Hydro - Lambton
5	S8- .7	"New" fly ash	
6	.8	Bottom ash	
7	S8-47.5	Primary sludge	Borg Warner
8	S8-49.3	Mine Tailings	Red Lake
9	S9-10.1	Carbon	Cabot Carbon
10, 11	S9-22.1, 2	Waste	Sarnia
12	S9-37.1	Iron foundry sand	
13	S9-64.1	Filtered plating sludge	North American Plastics
14	S9-69.1	Foundry sand	Massey Ferguson
15	.2	Liquid waste residue	
16	S9-76.1	Waste -	Cyanamid
17	S9-95.1	Sludge	Dofasco
18	S9-104.1	Fill	Chatham Grove
19, 20	S9-139.1, 2	Surface soil	Orchard St. Park, Kingston
21-24	S9-162.1-4	Paper waste	Abitibi
25	S9-199.12	Bag house dust	Ivaco
26	S9-222.1	Ditch	Atlas Steel
27	S9-223.1	Metal casting	Wingham
28	S9-240.1	Topsoil	Courtright
29	S9-264.1	Gray Tailings	Giant Yellowknife;
30	.2	Yellow Tailings	Giant Yellowknife
31	S0-66.1	Dewatered sludge	Oneida
32-34	S0-72.1-3	Lime - Treated sludge	Breslube
35-38	S0-80.1-4	Sub-division development	Toronto
39-40	S0-82.1-2	Steel waste	Taro Quarry
41	S0-93.1	Filter cake	Hobart
42	S0-108.1	Scrubber sludge	McCoy
43, 44	S0-159.1-2	Bag house dust	Burlington Steel
45, 46	S0-202.1-2	Insulation	Usarco
47-50	S0-203.1-4	Solidified waste	Frontenac,
51, 52	S0-214.1-2	Fixed sludge	Breslube
53	S0-215.1	Bag house dust	Usarco
54, 55	S0-217.1	Fixed sludge	Breslube
56, 57	S0-240.1-2	Fixed sludge	Breslube
58	S0-265.1	Solidified waste	Frontenac
59	S0-269.1	Foundry sand	Specialty Cast Metals
60	S0-273.1	Foundry sand - core	Fergusson Foundry
61	.2	- cupola bottom	
62	S0-275.1	Catalyst	Shell
63	S0-286.1	Cat cracker	Suncor
64	S0-309.1	Casting Floors	Stanton
65	.2	Scrubber settling tank	
66-68	S0-324.1-3	Steel making waste	Dofasco
69	S0-328.1	Metal Sludge	Ford
* 2A	S7-37:13-27	Arsenic wastes	Deloro

LEACHABILITY OF SOLID INDUSTRIAL WASTES

UNSATURATED FLOW COLUMN LEACH TESTS
WITH DISTILLED WATER

BY

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LABORATORY SERVICES BRANCH
ONTARIO MINISTRY OF THE ENVIRONMENT

JULY 1981

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ABSTRACT

Data from laboratory column leach tests on industrial wastes using distilled water in "unsaturated" flow is reviewed with respect to conformity with the penetration theory of diffusivity for transport of soluble species.

Ionic flux conformed to the theory for most ions tested for a range of types of industrial wastes, although there were a number of exceptions.

Data is presented graphically for various types of waste and for specific inorganic ions, conductivity and phenol. Some wastes could be considered inert on the basis of low leachability. Bag-house dust and some abandoned mine tailings samples had high leachability of toxic metals.

Factors leading to non-conformity with the penetration theory of diffusivity and limitations of the column leach test are discussed.

Some consideration is given to chemical factors controlling the mobilization of inorganic species.

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INTRODUCTION

Various procedures have been used for leach testing solid industrial wastes and, to date, no agreement has been reached by organizations such as the ASTM on a standardized test. Positive and negative aspects of different methods were reviewed recently by the author (Darcel, 1981). The column leach test currently used at the Central Laboratories (Inorganic Trace Contaminants Section) Ontario Ministry of the Environment was discussed in this review. It was pointed out that the "unsaturated" flow procedure with distilled water leach was intended to evaluate situations in which a waste would only be exposed to rain water. "Saturated" flow conditions would apply if the waste material was expected to be under water and/or was of low permeability. More severe leaching conditions, e.g. the use of acetic acid in the U.S. Environmental Protection Agency's "Extraction Procedure" test, would be required for industrial wastes to be co-disposed with municipal wastes.

Column leach tests have been used in this laboratory since 1974; however, the present procedure was standardized in 1978.

PROCEDURE

The procedure (Appendix II-Method A) consists essentially of percolating drop-wise 100g of the waste as received with distilled water in a 35mm I.D. column at a rate of 300ml/24 hours (a "cut"), collecting three cuts. The cuts are analyzed for various parameters as requested by the sampler plus pH and conductivity. In most instances, the permeability of the material is usually sufficiently high to permit "unsaturated" flow. In a few cases with low permeability, liquid forms above the upper surface, the material becomes "saturated" and leachate flow is reduced or even non-existent.

Some variability in test conditions is introduced due to differences in initial and final moisture contents and in the firmness and uniformity of packing the columns. However, there is sufficient standardization of conditions, at least for "unsaturated" flow, that it is possible to compare test results for different types of waste. It was assumed for this study that the leachate volume for each cut is 300ml; This is so for the second and third cuts but more of an approximation for the first cut, depending on the initial moisture content and water-holding capacity of the material.

Leachate is filtered through glass wool at the bottom of each column prior to analysis. The determination of components in the leachate, therefore, can include colloidal material or very fine particulates in some instances.

Metals are analyzed by atomic absorption spectrophotometry (AAS), usually after digestion with HCl/HNO_3 . In instances of clear leachate acidification prior to AAS rather than digestion is practiced. Anions are determined by auto-analyzer.

Most leach tests are run singly because of the heavy analytical work load produced by each leach. One test, however, was replicated in conjunction with an inter-laboratory comparison.

A sample of pulverized solidified steel manufacturing waste (No. 88) was tested in triplicate with consistent results for parameters tested in the three cuts. Unfortunately, amongst the metals tested, only molybdenum leached in significant concentrations. However, the leaching of this metal, traces of copper, pH and conductivity could be used as indicators of reproducibility (Appendix III). There was satisfactory agreement between triplicates and with the results of an inter-laboratory comparison with Ontario Research Foundation for this material.

In general, comparisons were made between concentrations in the different cuts for the various parameters to assess rate of leaching. For some wastes, concentrations in leachate were very low or below detection limits; in others they were relatively high, such as for metallic bag-house dust samples and some abandoned mine tailings.

Unfortunately, it was not possible to analyze for all parameters of interest. In most cases, the samples were considered routine and tested only for parameters requested by the sender. In some cases, leachate was tested for a range of parameters to determine if the material was inert ("clean fill") or to assess its suitability for landfilling. There was not, therefore, any comprehensive study of the leaching of any one parameter. Data is also minimal or lacking for some of the toxic metals, e.g. mercury, and environmentally significant anions such as nitrate, fluoride, borate and phosphate.

The majority of tests were conducted under saturated flow conditions for which concentrations of ions in leachate for different wastes can be compared directly. For less permeable materials with reduced and variable flow rates, some comparison is still possible using mass rather than concentration ($\mu\text{G} = \text{mg/L} \times \text{mL}$).

Samples have been identified by consecutive numbers, laboratory numbers and description in Appendix I. Source information and copies of individual leach test reports are available from the author on a restricted basis to protect confidentiality of the private sector.

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PENETRATION THEORY OF DIFFUSIVITY

An attempt was made to determine if column leaching under unsaturated flow conditions followed a physical law. In other studies, distilled water shake test data for total dissolved solids from stabilized flue gas desulphurization wastes could be related to the penetration theory of diffusivity (Taub & Roberts, 1978).

Higbie (1935) envisaged turbulent flow producing eddies with transient entities or "parcels" with molecular movement. Concentration is a function of the reciprocal of the square root of time according to this theory (Bird et al, 1960). A straight line relationship should be obtained between the average ionic flux and the square root of the diffusivity and inversely with the square root of time. It is possible to calculate "effective diffusivities" for different materials.

If it is assumed that for unsaturated flow in the Ontario Ministry of the Environment tests volume and flow rate are constant, the cumulative sum of the concentrations of any parameter in the successive cuts can be related to the flux for that ion. Conformity with the penetration theory of diffusivity can be tested graphically by plotting the cumulative sum of each ion and phenol concentration in mG/L against $\frac{1}{\sqrt{T}} \times 10^3$ for 24, 48 and 72 hours. A similar

plot was undertaken for conductivity to explore the relation that conductivity, at least for some natural waters, is related to total dissolved solids and, thereby, total ionic concentration.

The graphical plot test for conformity with the penetration theory of diffusivity was conducted for column leach tests with distilled water using different types of industrial solid wastes. Similar plots were also drawn for each parameter considered independantly of sample type. Some of the data was factored to permit plotting several orders of magnitude on the same graph.

In some tests, concentrations were below detection limits; in others, concentrations in the three cuts obviously did not follow the penetration theory of diffusivity. The data was not plotted graphically for these situations.

Results of some of the more interesting types of waste are discussed below.

RESULTS

A. SOLID WASTES

A1. Metal Bag-house Dusts

Bag-house dust samples from iron foundries and some other metal processing operations were of interest in that they were very high in iron although a negligible amount was leachable. Chromium, nickel, and copper were also relatively stable.

Leachable cadmium was the most potentially serious environmentally. Relatively high concentrations persisted through third cut in Sample No. 53 (Table I). The zinc concentrations was very high in the first cut, but dropped off rapidly although still high in the third cut.

Lead was of interest in Sample No. 25 as concentrations increased during leaching and remained high through the third cut. A high concentration was obtained in the third cut in Sample No. 44 (perhaps because the metal was present in colloidal state as discussed later).

Molybdenum showed the highest percentage release, particularly in the first cut, but persisting through the third.

The pH was variable, ranging from slightly below neutrality (Sample Nos. 53 & 43) to moderately to strongly alkaline (No. 25). Conductivity was also relatively high in No. 25.

There was good conformity with the penetration theory of diffusivity for some metals and conductivity (Figure I). Lead was a marked exception. An attempt to reduce surface area by pelletizing in the presence of Portland Cement (No. 85) did not prevent the leaching of lead or molybdenum although it was reduced. Leaching did not follow the penetration theory of diffusivity for either metal (concentration increasing instead of decreasing, especially for lead).

Bag-house dusts from a steel manufacturing operation (No. 86) contained high concentrations of Zn, Pb and Cd which were readily leachable in a column leach test. Concentrations were exceptionally high in the first cut (much higher than one would expect using the penetration theory, in relation to cuts Nos. 2 and 3).

It is suggested that the high initial concentration of metals in the dusts in conjunction with the large surface area of the finely divided particles were major factors accounting for the high leachability. Even in pelletized form leaching occurred, no doubt because the pellets were permeable.

TABLE I
DISTILLED WATER COLUMN LEACH
BAG-HOUSE DUSTS

#53	S ^o 215-1	Concentrations MG/L		
	Cut 1	Cut 2	Cut 3	
Zn	2200	820	70	
Ni	1.8	.71	.40	
Pb	1.9	8.5	7.9	
Cd	490	93	81	
pH	6.6	7.2	6.7	
Cond mmhos				
x1000	26	4.8	3.3	

#25	S9-199-12		Cut 1	Cut 2	Cut 3
	Total %				
Zn	15		.89	.24	.16
Cu	0.2		.18	.02	.03
Pb	8.1	170(.63%)*	170(.63%)	110(.41%)	
Cd	.06		.04	.01	.01
Cr	.15		.45	<.06	<.06
Fe	24		<.2	<.2	<.2
pH			11.8	11.5	11.4
Cond mmhos					
x1000			67	18	16

* percentage of total leached

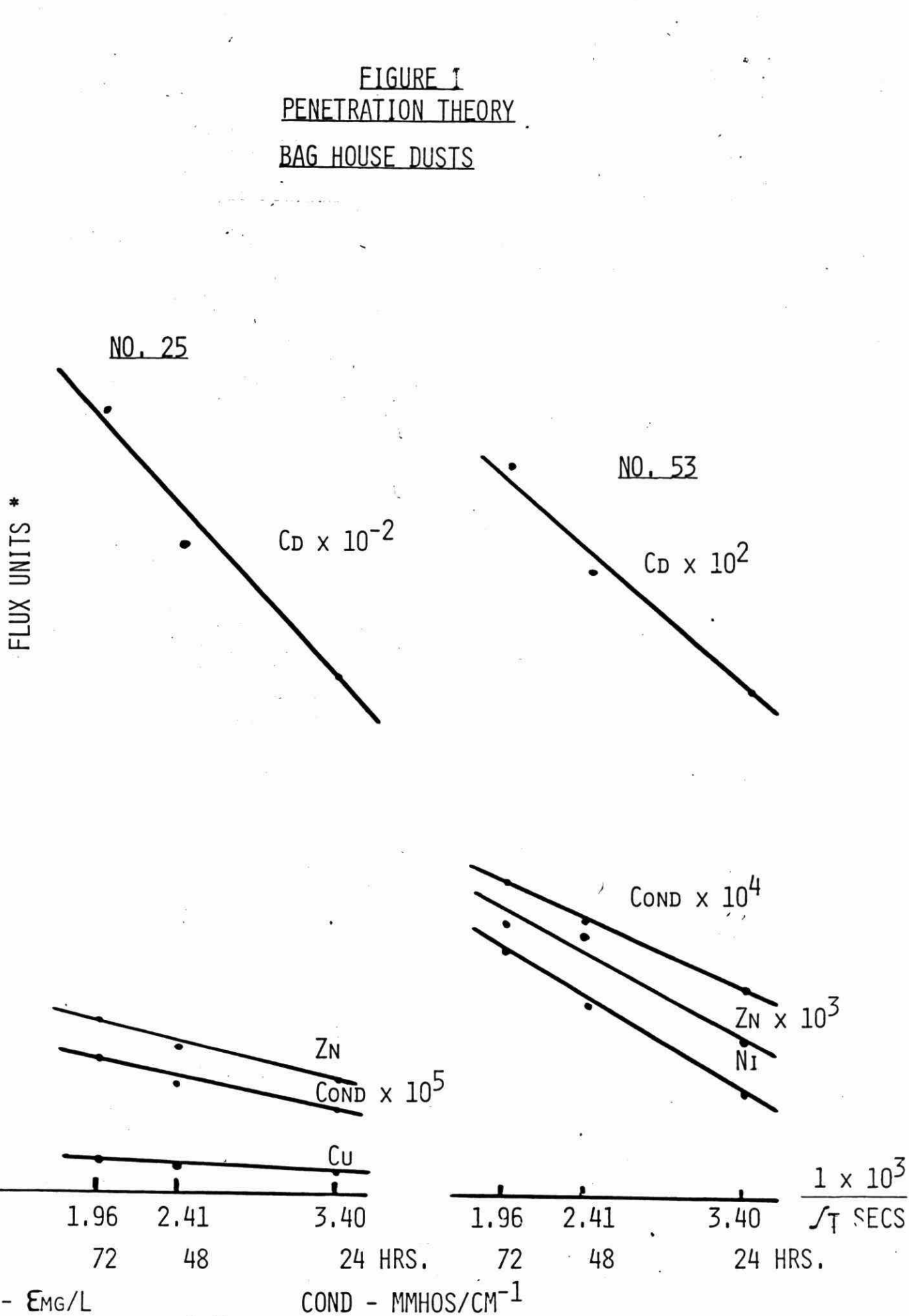
#43	S ^o 159-1		Cut 1	Cut 2	Cut 3
	Total %				
Zn	18		32	.09	.10
Cu	.29		.11	.06	.04
Ni	.03		.06	.06	.06
Pb	4.2		2.6	1.7	2.3
Cd	.097		45	.43	.13
Cr	.24		.06	.06	.03
Mo	.04		.05	.04	.04
Fe	26		.2	.2	.2
pH			6.8	7.2	7.1
Cond mmhos					
x1000			24	7.6	1.8
Colour			Yellow	Pale yellow	

#44	S ^o 159-2		Cut 1	Cut 2	Cut 3
	Total %				
Zn	15		.10	.09	1.2
Cu	.43		.14	.14	.23
Ni	.04		.06	.06	.06
Pb	4.1	9.4(.07%)**	44(.32%)	90* (.66%)	
Cd	.070		.41	.02	.02
Cr	.23		1.0	.06	.06
Mo	.012	3.5(8.8%)	1.5(1.6%)	.36(1.0%)	
Fe	29		.2	.2	.2
pH			8.1	10.4	8.0
Cond mmhos x1000			28	2.0	1.5

* dispersed colloidal state

** figures in parenthesis represent percentage of total leached

FIGURE 1
PENETRATION THEORY
BAG HOUSE DUSTS



A2. Mine Tailings and Metal Refinery Wastes

High concentrations of Fe, Cu, Zn and As were obtained in the first cut from a sample of "grey" tailings from the abandoned Giant Yellowknife mine (No. 29). The high copper concentration persisted through the second cut. Concentrations were much lower in "yellow" tailings (No. 30). The pH of leachate was low for both grey and yellow tailings and can be considered the main factor causing the high leachability. In contrast, the reaction was basic for an abandoned silver smelter mine tailings (No. 2) and there were low concentrations of metal in leachate, in spite of high hot acid extractable metal content (Table II).

Leaching of several metals followed the penetration theory (Figure II). In all three samples there was close agreement for conductivity.

Highest concentrations of water-extractable As, Co, Ni, and Cu were found in various samples of refinery waste at the abandoned Deloro site (Sample series 2A). There was good agreement with the penetration theory of diffusivity for all four metals at the high levels of concentrations (to be presented in a separate report).

TABLE II

DISTILLED WATER COLUMN LEACH

Mine Tailings

I Acid Tailings Giant Yellowknife

#29	<u>Grey Tailings</u>		<u>Concentrations MG/L</u>	
	<u>S9-264-1</u>	<u>Cut 1</u>	<u>Cut 2</u>	<u>Cut 3</u>
	Zn	160	1.3	0.4
	Cu	260	310	0.6
	Ni	1.2	1.1	.06
	Pb	2.1	3.1	4.1
	As	65	8.9	1.8
	Fe	930	19	5.1
	pH	2.2	3.0	3.2
	Cond mmhos			
	x 1000	40	18	9.2

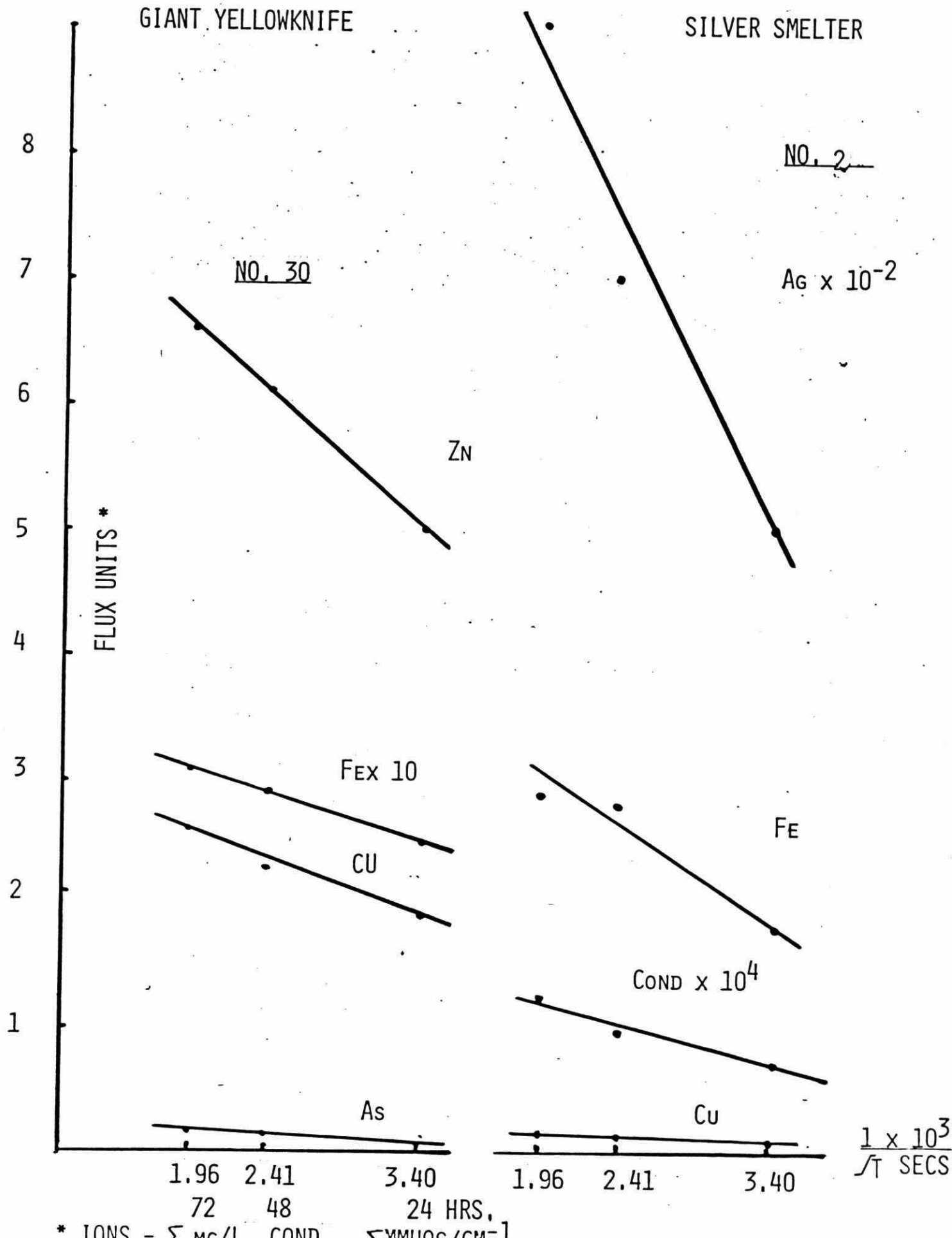
#30	<u>Yellow Tailings</u>			
	<u>S9-264-2</u>	<u>Cut 1</u>	<u>Cut 2</u>	<u>Cut 3</u>
	Zn	5.0	1.1	0.5
	Cu	1.9	0.4	0.3
	Ni	0.2	<0.06	<0.06
	Pb	< .07	<0.06	<0.06
	As	0.09	0.05	0.01
	Fe	25	3.8	2.1
	pH	2.3	2.6	2.8
	Cond mmhos			
	x1000	16	8.2	4.0

#II Basic Tailings
Silver Smelter - Cobalt

#2	<u>S7-31-129</u>	<u>Total*</u>	<u>Cut 1</u>	<u>Cut 2</u>	<u>Cut 3</u>
	Zn	3500	0.02	0.07	0.02
	Cu	1200	0.09	0.03	0.04
	Ni	2800	< 0.04	<0.04	<0.04
	Pb	1600	< 0.06	<0.06	<0.06
	Co	9500	5.4	--	0.22
	As	48000	0.99	1.4	1.2
	Ag	110	0.05	0.02	0.02
	Fe	35000	1.8	1.0	0.08
	pH		8.4	8.5	8.9
	Cond mmhos	X1000	7.2	3.0	2.4

* Concentration ug/g HCl/HNO₃ extractable.

FIGURE II
MINE TAILINGS



A3. Metal Sludges

Metal contents were high (in the percent range) in some metal plating sludges. Leachable metal, except for Ca, tended to be low, at least in the second and third cuts. The pH was high, ranging from 9 to 12. In one sample (No. 13) with 15% Cu, there was only 0.1 mg/L Cu in the third cut. There was close conformity with the penetration theory of diffusivity for some metals and conductivity (Figure III).

Metal sludge filter cake containing high concentrations of Zn, Ni, Cr, and Sn (No. 41) was stable to water leach with concentrations of metals in the leachate below detection limits, except for traces of Ni and Cr.

Similarly a scrubber sludge, high in Fe, Pb, Zn, Cu and Sn (No. 42), yielded a leach with most metals below detection limit for most metals except for Zn (1-6mg/L) and traces of Pb, Cu and Cd.

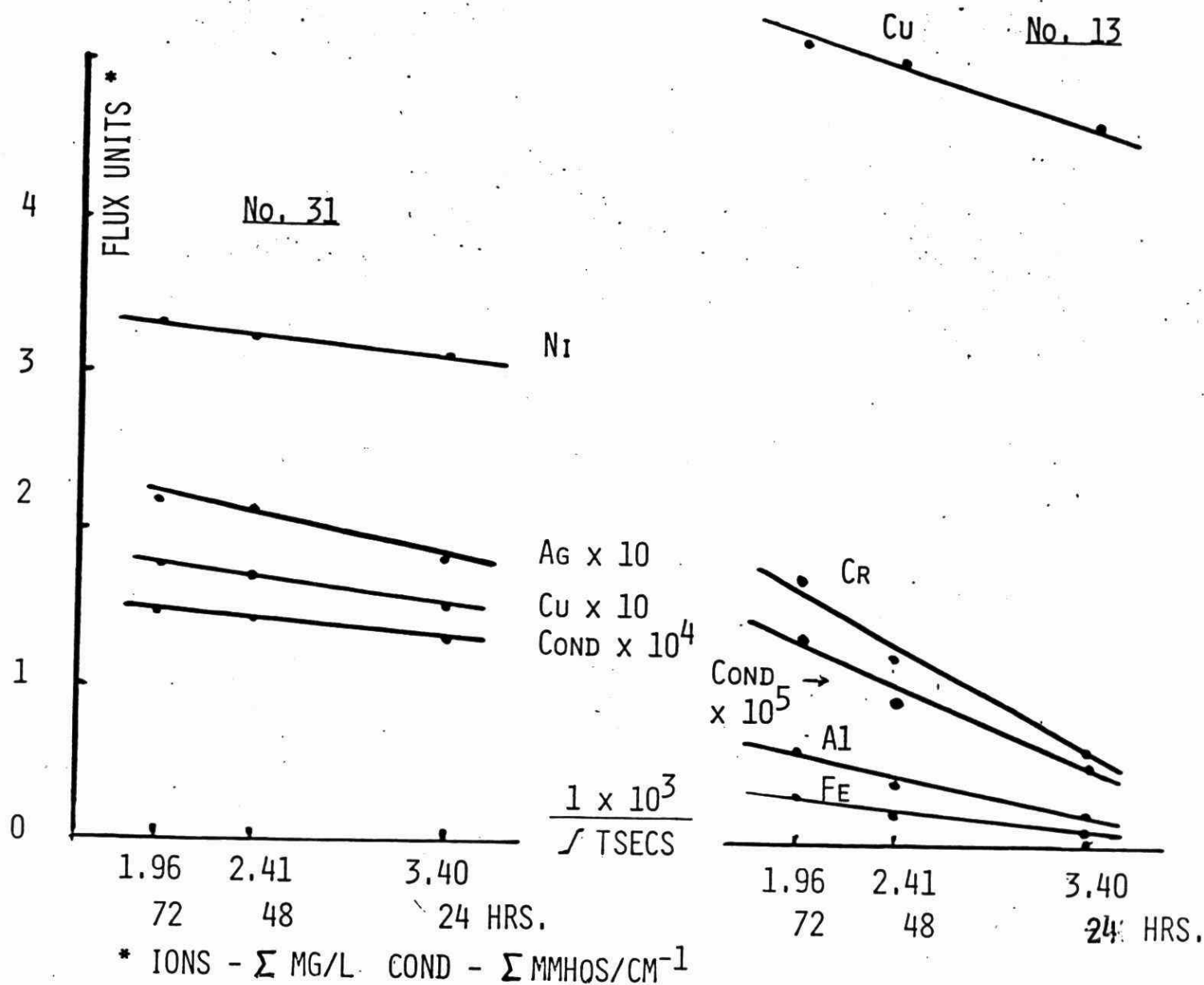
Sludge from a metallic waste lagoon (No. 69) was stable to water leach with Zn, Cu, Ni, Pb, Cd, Co and Cr undetectable in leachate. The materials in the column tended to become less permeable during the duration of the test, becoming impermeable in cut 2.

TABLE III

DISTILLED WATER COLUMN LEACH
METAL SLUDGES

#31	<u>S^o66.1</u>			
	Total	Concentrations MG/L		
	<u>%</u>	<u>Cut 1</u>	<u>Cut 2</u>	<u>Cut 3</u>
Cu	20	15	1.8	0.6
Ni	2.7	3.1	0.1	0.1
Ag	0.02	18	0.3	0.06
Zn	7.5	0.03	<0.02	<0.02
pH		9.6	9.8	9.1
Cond x 1000		13	1.2	0.5
#7	<u>S8.47.5</u>			
		<u>Cut 1</u>		<u>Cut 2</u>
Zn		1.7		0.2
Cu		0.3		0.1
Fe		0.7		0.2
Ca		130		16
Mg		15		3
#13	<u>S9.64.1</u>			
	<u>%</u>	<u>Cut 1</u>	<u>Cut 2</u>	<u>Cut 3</u>
Cu	15	4.6	0.4	0.1
Cr	3.0	0.6	0.6	0.5
Al	0.06	0.2	0.2	0.2
Fe	0.7	0.1	0.1	0.1
Ca	12	780	640	510
pH		12.2	12.2	12.2
Cond x 1000		52	39	43
Cd, Cu, Pb, Mn, Mg, Mo, V, Zn, Ni <0.1 mg/L				

FIGURE III
METAL SLUDGE



A4. Foundry Sands

Metal concentrations in leachate from Nos. 12 and 14 were low, except for Ca and Mg, with some below detection limits. The reaction was basic. Concentrations in the third cut tended to be at the same level as the second cut; hence conformity, with the penetration theory was poor. Conductivity was high in both samples and values followed the penetration theory. Other foundry sands were even more inert and are discussed later (Nos. 27, 59, 60, 61, 64, 68 and 70).

TABLE IV

DISTILLED WATER COLUMN LEACH
FOUNDRY SAND

#12	<u>S9.37.1</u>		
	Concentrations MG/L		
	<u>Cut 1</u>	<u>Cut 2</u>	<u>Cut 3</u>
Ca	32	23	29
Mg	6.5	9	6.2
Sr	0.3	0.4	0.3
Fe	0.4	0.5	0.8
pH	8.1	8.2	8.3
Cond x 1000	2.6	2.4	1.8
Zn, Cu, Pb, Cd, Mo, Ni	<0.1 mg/L		
#14	<u>S.9.69.1</u>		
	<u>Cut 1</u>	<u>Cut 2</u>	<u>Cut 3</u>
Ca	22	25	22
Mg	12	10	8
Mn	0.5	0.2	0.2
Al	0.7	0.4	0.4
Zn	0.6	0.4	0.4
Pb	0.3	0.2	0.1
pH	8.2	8.3	8.1
Cond x 1000	3.9	2.4	2.0
Cu, Cd, Cr, Mo, V, Ni	<0.1 mg/L		

A5. Fly and Bottom Ashes

Samples from the Lambton generating station were tested (Nos. 4 to 6). Of interest (but not unexpected because of exposure to rain for different periods) was the high concentration of leachable sulphate in "new" fly ash compared with "old" fly ash (Table V). Plots of both chloride and sulphate showed good agreement with the penetration theory of diffusivity (Figures XIX and XX).

Calcium concentrations were high in the first cut, dropping off rapidly by the second cut.

TABLE V

<u>DISTILLED WATER COLUMN LEACH</u>			
<u>FLY AND BOTTOM ASH</u>			
<u>Lambton Generating Station</u>			
#4	<u>S8.41.6 "Old" Fly Ash</u>		
	Concentrations MG/L		
	<u>Cut 1</u>	<u>Cut 2</u>	<u>Cut 3</u>
Ca	430	57	50
Mg	3.2	<0.025	<0.25
Zn	0.02	<0.02	0.02
SO ₄	980	120	80
Cl	290	50	40
#5	<u>S8.41.7 "New" Fly Ash</u>		
	<u>Cut 1</u>	<u>Cut 2</u>	<u>Cut 3</u>
Ca	560	590	180
Mg	0.25	0.5	0.25
Zn	<0.02	<0.02	<0.02
SO ₄	1700	1500	420
Cl	50	20	10
#6	<u>S8.41.8 Bottom Ash</u>		
	<u>Cut 1</u>	<u>Cut 2</u>	<u>Cut 3</u>
Ca	220	30	18
Mg	13	2.5	8.2
Zn	0.10	0.04	0.02
SO ₄	600	100	50
Cl	40	10	10

A6. Solidified Wastes

Column leach tests with distilled water were used extensively to evaluate solidified waste pickle liquor. The results from some of these tests were reviewed previously by the author (Darcel, 1979). Since various processes were operative to minimize metal migration (e.g. precipitation, cation exchange) agreement with the penetration theory was usually poor (Sample Nos. 47 to 50). In a batch with very high concentrations of Fe, Zn, Cr, Pb, Cu and Ni (No. 58), there were significant concentrations of Cu, Ni and some Fe in the first cut (24, 7.5 and 3.1 mg/L respectively) decreasing rapidly in the subsequent cuts. Concentration changes followed the penetration theory of diffusivity. Concentrations of Cr and Pb were close to the detection limit

Leach tests with solidified waste were normally run using air-dried lumps of the material. Under these conditions, permeability was good, permitting unsaturated flow. However, if the material was packed into the column "as-is" while still damp, permeability was low and a reduced quantity of leachate (or none) would be produced under saturated flow conditions.

Dofasco have been conducting leach tests on solidified waste using the M.O.E. unsaturated flow procedure (Ertel, 1981). Metals were immobilized but some leaching of fluoride was evident but could be minimized by using the optimum proportions of cementing agent. In a test at M.O.E. (No. 66) metals were not released. The pH was high (pH 12) and conductivity elevated (about 4500 mmhos) in the three leachate cuts.

Control and test batches of solidified "fixed" steel making waste, including bag-house dust with high concentrations of Pb and Cd (Nos. 87-89), were subjected to column leach tests with distilled water. Leaching of lead occurred initially for several cuts using relatively fresh "as-is" material. Lead was "fixed" when the test was run using one month old ("cured") air-dry pulverized material. Some molybdenum was leached however, at a rate following the penetration theory.

Leach tests were also conducted on lime treated waste oil sludges (Nos. 32-34, 51-52, 54-57). Heavy metal concentrations tended to be low, except for lead, determined in one sample (No. 32). Phenol concentrations were high and, in some samples, leaching followed the penetration theory of diffusion. One sample (No. 56) became impermeable by the third cut.

Useful information can be gained on stabilized wastes, particularly those based on lime, by conducting titrations with acid. This was undertaken for steel-manufacturing waste (No. 88). The changes in pH with increments of sulphuric acid addition, plotted graphically, indicated the buffering capacity of the waste and reserve of alkalinity. By withdrawing and analyzing aliquots for metals of interest, e.g. Pb and Cd, during the titration it was possible to follow the effect of increasing acidity on the release of toxic metals.

A7. Inert Wastes

Some relatively "inert" materials were tested for leachability. A sample of "fill" (No. 18) and a sludge from an oil treatment plant (No. 76) contained low concentrations of HCl/HNO₃ extractable metals. These materials, therefore, were not tested further, except for leachable phenol in No. 18 (also found to be low).

A waste buffing compound (No. 3) was found to be inert with respect to the leaching of heavy metals, with concentrations below detection limits except for Ni. Concentrations for this metal were anomalous (increasing with leaching).

A ditch sample, containing steel-making waste (No. 26) was found to be "inert" with respect to the leaching of Cu, Ni, Pb, Zn and in spite of moderately high original content of these metals. Conductivity was also low, and its change with the progression of cuts followed the penetration theory of diffusivity fairly closely.

Some foundry sands were "inert" as indicated by the low conductivity of the leachates (Nos. 60, 61) and metal concentrations below detection limits; also low phenol (Nos. 27, 59, 64, 68 and 70). In one instance (No. 26) the sand became impermeable after the second cut. A slag and scrubber dust (No. 65) was also inert.

Leachate from a manufacturing waste holding area in Niagara Falls (Nos. 71 to 75) was almost free of heavy metals (except for Cr in the first cut of No. 74). The high conductivity of the first cut of some of the samples was rapidly reduced by the second cut. One of the samples (No. 71) was impermeable after the first cut. A lime waste in Sarnia (Nos. 77 to 81) was free of heavy metals in leachate except for traces of copper.

The high pH of most leachates (up to pH 12) and high conductivity (up to 6000 mmhos) provided grounds for considering this material as reactive rather than inert, although heavy metal concentrations were low.

A waste carbon (No. 9) was found to be inert with respect to the leaching of metals, conductivity and pH. Core sand and dust and sand from a brass smelter and manufacturing operation (Nos. 82 and 84) generated clean leachate with heavy metals concentrations below detection limits, relatively low conductivity and moderately high pH. Leachate from a sand-blasting waste from the same factory (No. 83) was also free of heavy metals except for moderate concentrations of lead (8.5 mg/L dropping to 0.11 mg/L in the third cut). Leaching of lead conformed to the penetration theory. Conductivity also agreed with the theory for Nos. 82 and 83. An insulation waste (Nos. 45 and 46) was also found to be inert with respect to metal concentrations and conductivity of leachate. Traces of monomeric vinyl chloride were detected in head gas above the original sample.

Similarly, an oil refinery spent catalyst containing V and Ni (No. 62) and a "cat cracker" (No. 63) were stable to water leach.

A8. Soils

Soil samples from a construction site in Toronto (Nos. 35 to 38) were checked for leachability because of suspected contamination. Only one leachate cut was taken. Toxic metals were undetected in the leachate; of interest, however, were low concentrations of Fe and Al (4-8 mg/L) at a pH 7.8 - 8.0. Surface "soil" samples from Kingston (Nos. 19 and 20), contaminated with old metal refining wastes, had high concentrations of leachable arsenic and some mercury.

B. INDIVIDUAL PARAMETERS:

Conformity with the penetration theory of diffusivity was tested for a range of cations, anions, phenol and conductivity (for total dissolved solids). For some parameters, unfortunately, there was little data, as discussed earlier.

It is of interest to note that for all parameters checked there were instances of conformity and exceptions to the penetration theory. Exceptions were of two types: in one type essentially all of the soluble component was released in the first cut; in the other type concentrations increased rather than decreased (as expected for the penetration theory). This occurred principally with iron. Behavior of the various parameters is discussed below. Metals commonly considered to be toxic are considered individually; other metals with chemical similarities and anions are discussed in groups.

Molybdenum and vanadium are grouped together because they both form oxy-anions with similar properties. Manganese, iron and aluminum are relatively abundant in soils and readily form complex hydroxides which can play a significant role in the attenuation of toxic species. Calcium and magnesium are of particular interest in the control of pH and thereby the susceptibility to leaching of most toxic ions. Chloride and sulphate are normally present in natural waters. Attenuation in soils is less than for metals, particularly for chloride.

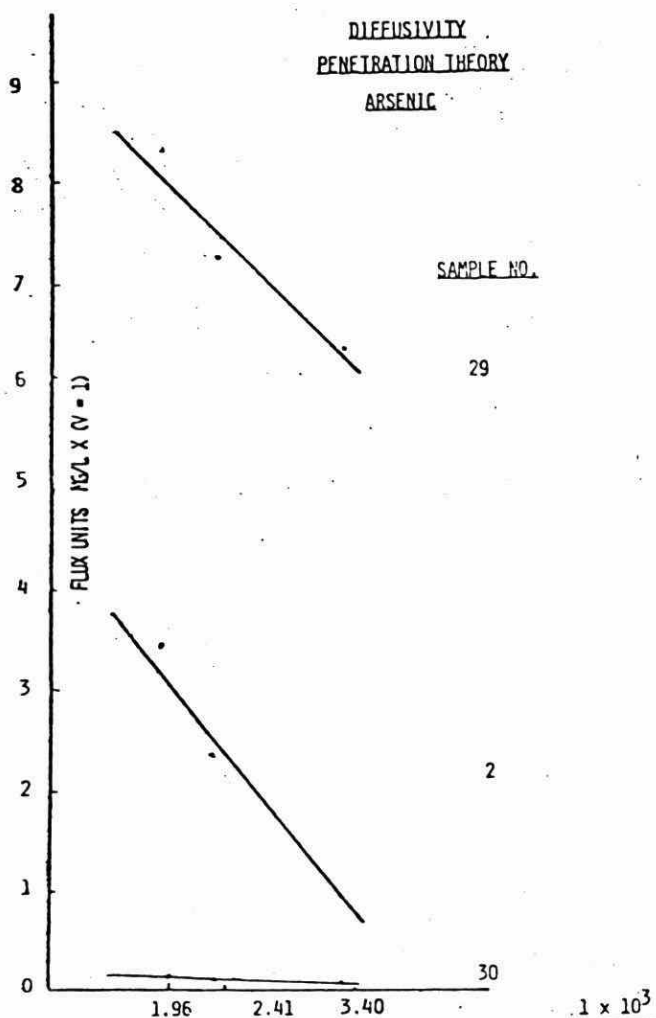
B1. ARSENIC

Relatively high concentrations of arsenic were leached from the sample of grey tailings from Giant Yellowknife (No. 29) with much lower concentrations leached from the yellow tailings sample (No. 30). In both cases, movement of arsenic conformed to the penetration theory of diffusivity. Good agreement with the theory was also obtained for sample No. 2

A very extensive series of column leach tests with distilled water was conducted on Deloro wastes in 1977 (Series 2A). In some samples there was very extensive leaching of arsenic and in others Co, Cu and Ni. In several cases, leaching of arsenic and other metals followed the penetration theory of diffusivity, even at very high concentrations.

These wastes are currently the focus of field and laboratory studies aimed at their stabilization. A separate report will be prepared on leach testing for arsenic, as discussed earlier.

FIGURE IV



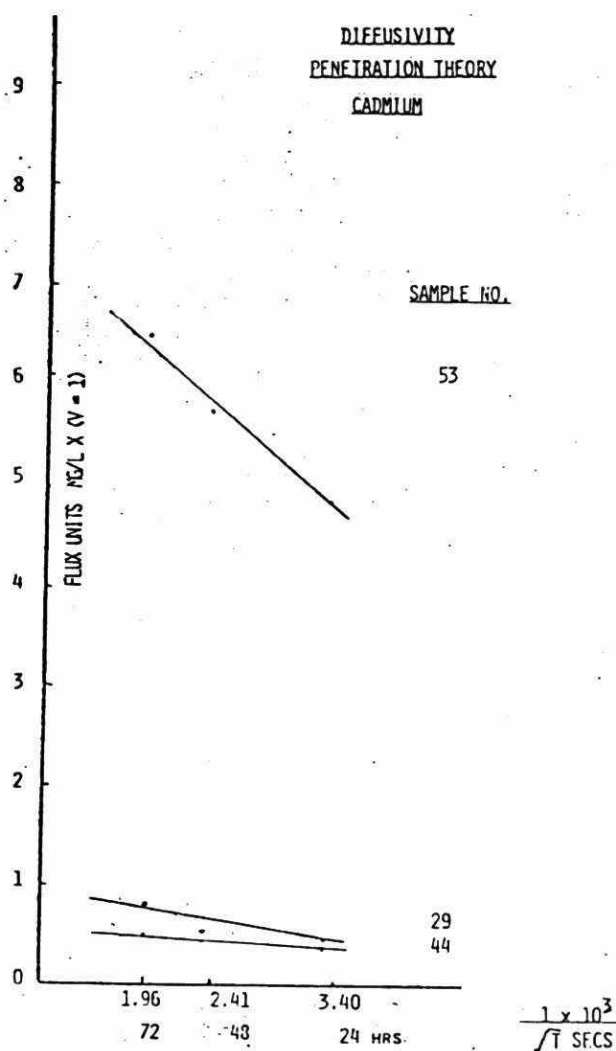
B2. CADMIUM

Cadmium was present in relatively high concentrations and mobile in some metal processing bag-house dust samples (Sample Nos. 53 & 43). There was close agreement with the penetration theory of diffusivity for No. 53 but there was poor agreement for No. 43.

Small amounts of cadmium were leached from grey and yellow tailings from Giant Yellowknife (Samples Nos 29 & 30). Leaching also fitted the penetration theory.

Low concentrations of cadmium were also leached from a scrubber sludge (No. 42) with concentrations increasing in the three successive cuts (0.03 to 0.08 mg/L), deviating from the penetration theory.

FIGURE V

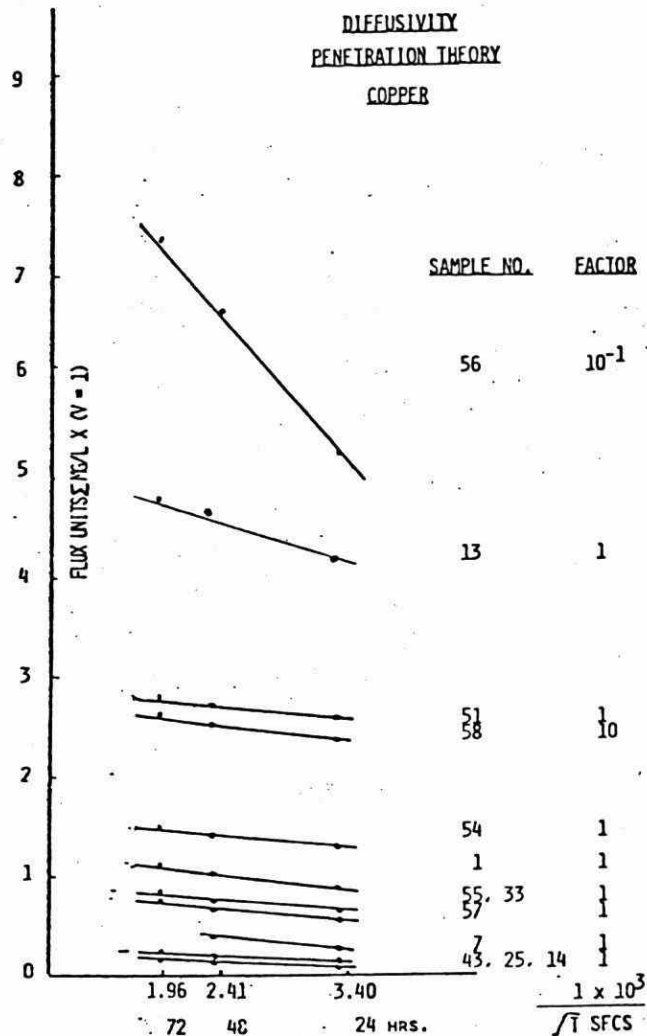


B3. COPPER

There was close agreement with the penetration theory of diffusivity for most of the samples tested over a wide range of extractable copper and types of waste. These included plating sludges (Nos 1, 7, & 13), solidified plating (Nos 54, 55 & 58), and oil wastes (Nos 54-57), bag-house dusts (Nos 25,43) and foundry sand (No. 14).

Some materials did not appear to follow the penetration theory, such as a buffing compound (No 2), grey tailings (No 29), core foundry sand (No 60) and catalyst (Nos 62 & 63).

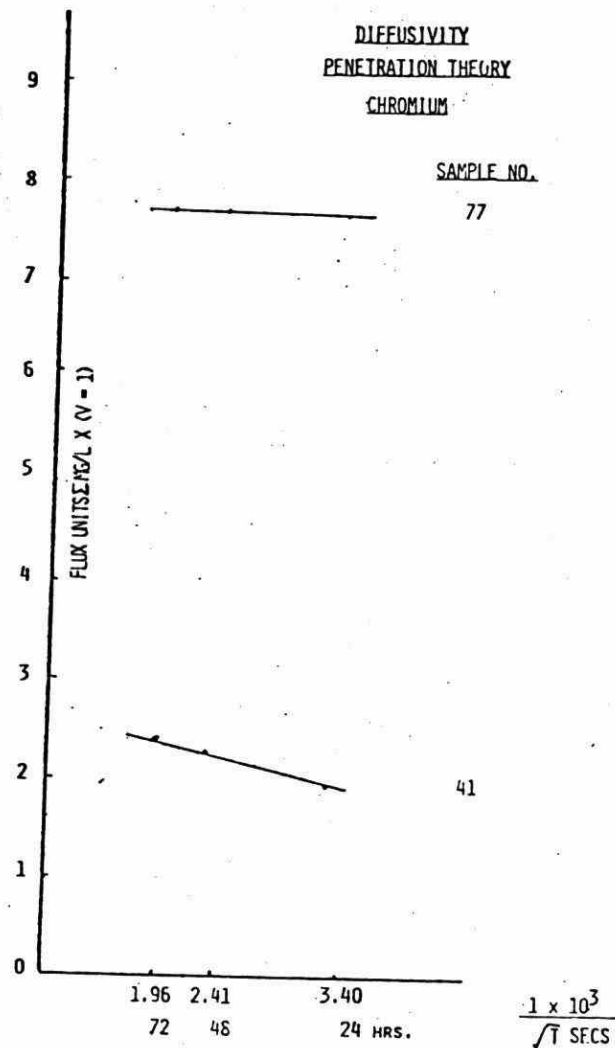
FIGURE VI



B4. CHROMIUM

Leaching of chromium was not observed for most samples. There was good agreement with the penetration theory for a filter cake (No 41). In a second sample (No 77) conforming with the theory almost all of the chromium was released in the first cut. There were some exceptions to the theory, such as some "fixed" oil sludges (Nos 51, 5 , 55) and insulation waste (Nos. 45 & 46).

FIGURE VII

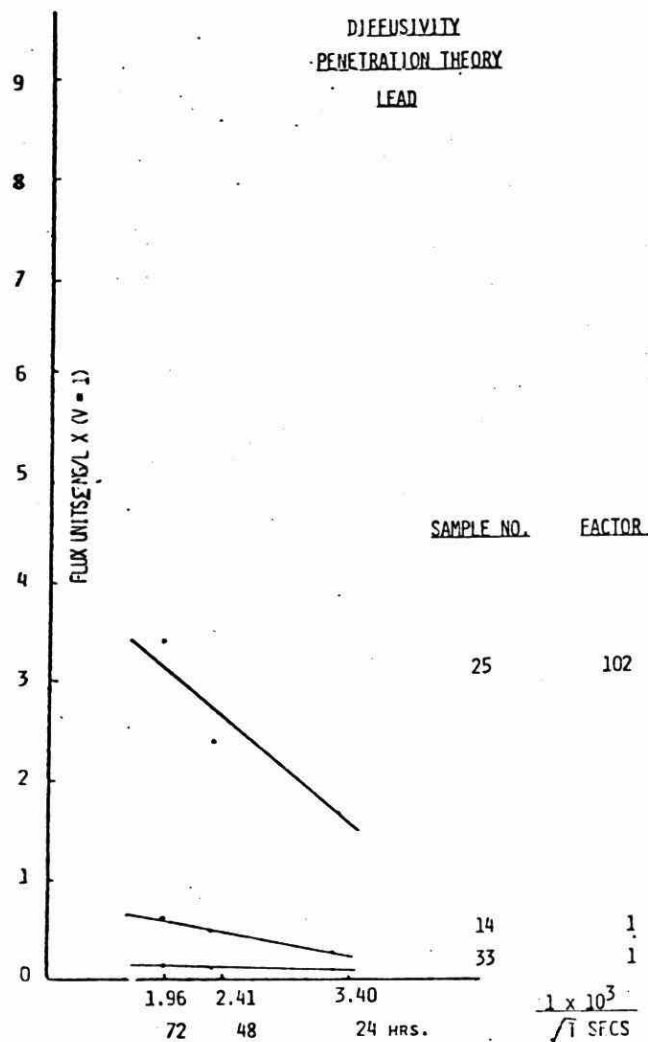


B5. LEAD

High concentrations of lead were leached from a bag-house dust sample (No. 25) with reasonable agreement with the penetration theory. Good agreement was obtained for lower concentrations of extractable lead from a foundry sand (No. 14). In a lime-treated sludge (No. 33) the small amount of extractable lead was removed in the first cut.

It is of interest that lead in some metallic bag-house dusts (Table I) did not follow the penetration theory and the suggestion was made that at least in one of the samples (No. 44) lead was in colloidal state in the leachate.

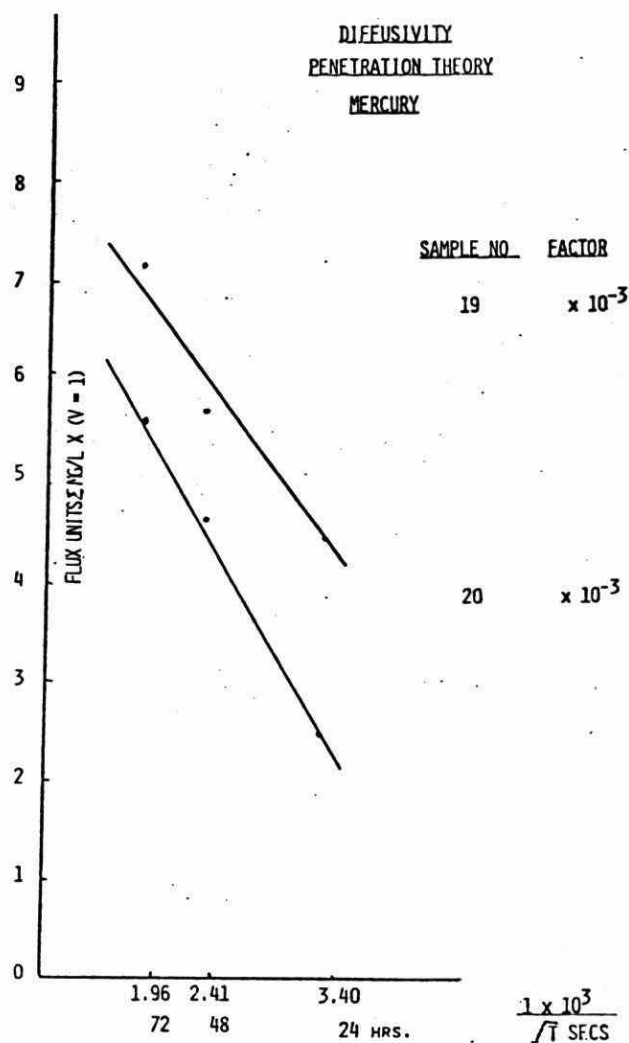
FIGURE VIII



B6. MERCURY

Mercury was detected in leachates from two surface soil samples from Orchard Street Park, Kingston (Nos 19 & 20). Even at the low concentrations obtained ($\mu\text{g/L}$ level) there was good agreement with the penetration theory of diffusivity.

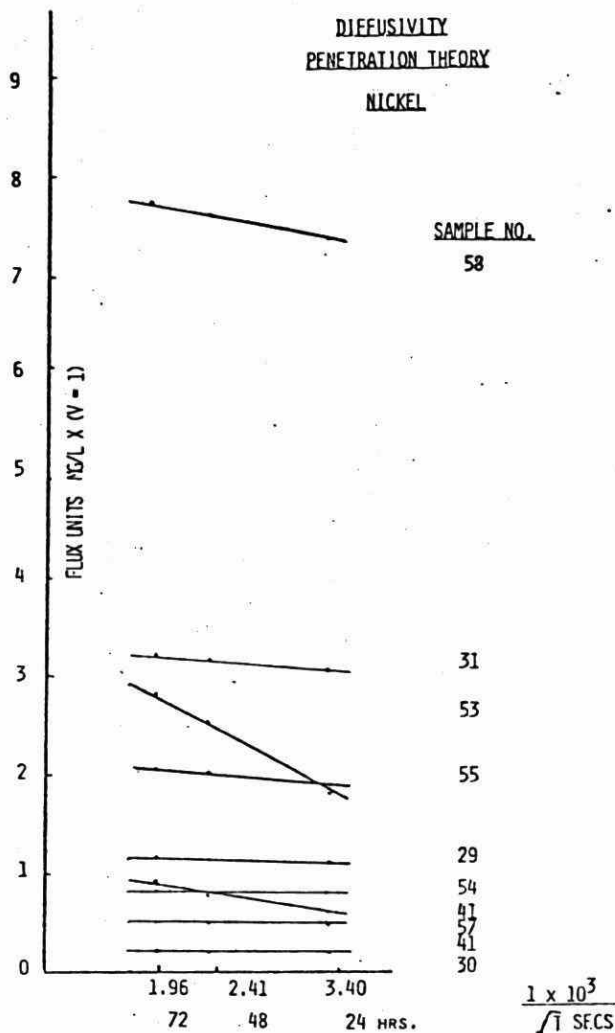
FIGURE 1X



B7. NICKEL

An appreciable amount of nickel was leached from a batch of solidified plating waste (No 58). Similarly, nickel was leached from a bag-house dust (No 53), a fixed oil sludge (No 55), and metal sludges (Nos 31 & 41). Leaching followed the penetration theory of diffusivity. In several other cases, almost all the nickel was leached in the first cut, e.g. tailings (Nos 29 & 30), and a fixed oil sludge (No. 57) as indicated by a horizontal line.

FIGURE X

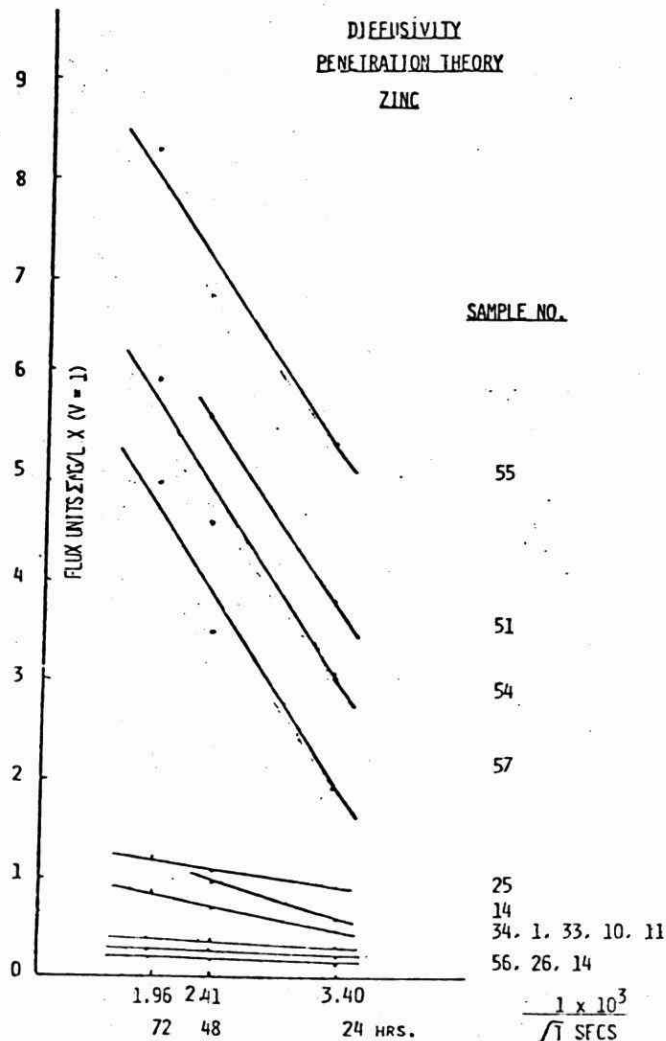


B8. ZINC

There was a strong agreement with the penetration theory of diffusivity for a number of samples, such as the fixed oil sludges (Nos. 33, 34, 51, 54, 55, and 57), bag-house dust (No. 25), and metal hydroxide waste (No. 1). In some samples with low extractable zinc, most of the zinc was extractable in the first cut (Nos. 14, 26, 6).

There were many exceptions to the penetration theory with zinc such as bag-house dusts (Nos. 43, 44, 53), fixed oil sludges (Nos. 51 and 52), scrubber sludge (No. 42), cat cracker (No. 63) and insulation waste (Nos. 45, 46).

FIGURE X1



B9. MOLYBDENUM AND VANADIUM

MOLYBDENUM

The leaching of molybdenum was noted with a bag-house dust (No. 44) and steel-making wastes (Nos 87-90). With these samples, concentrations of Mo in the leachate cuts followed the penetration theory (Figure XII). On the other hand, with a sample of bag-house dust pelletized with Portland Cement (No. 85) leaching of Mo still occurred but did not fit the theory (concentrations increased from cuts Nos. 1 through 3).

Molybdenum is of interest in that, unlike most metals, it tends to become soluble in basic medium (pH's ranged from 8 to 12 in the samples tested).

VANADIUM

The leaching of vanadium occurred with a refinery spent catalyst (No. 90) with concentrations decreasing in successive cuts, agreeing fairly well with the penetration theory (Figure XII). Other metals, such as Ni, Pb and Fe which were also present in relatively high concentrations in this sample, did not leach at the pH of the leachate (pH 7.4-7.2).

It is of interest to note that in another sample of spent catalyst containing approximately the same level of HCl/HNO₃ extractable vanadium (No. 62) the metal did not leach (< 0.1 mg/L) although the pH of leachate was of about the same (pH 7.0-7.2.)

DIFFUSIVITY-PENETRATION THEORY

FIGURE XII
MOLYBDENUM

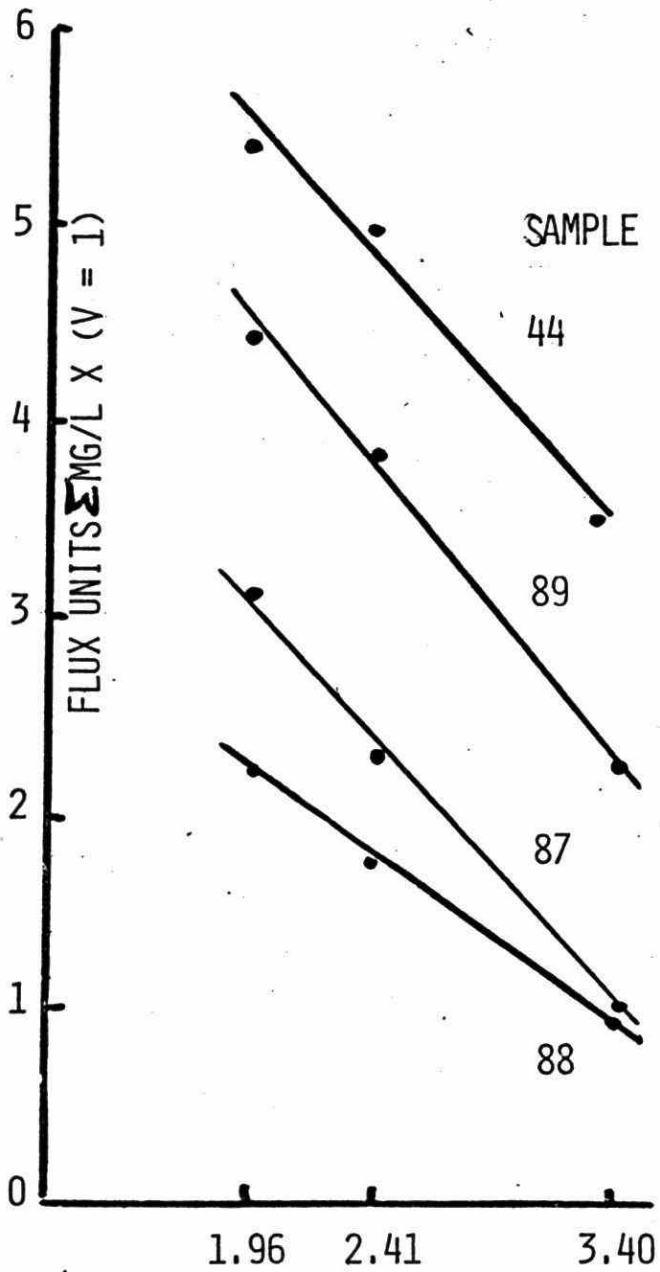
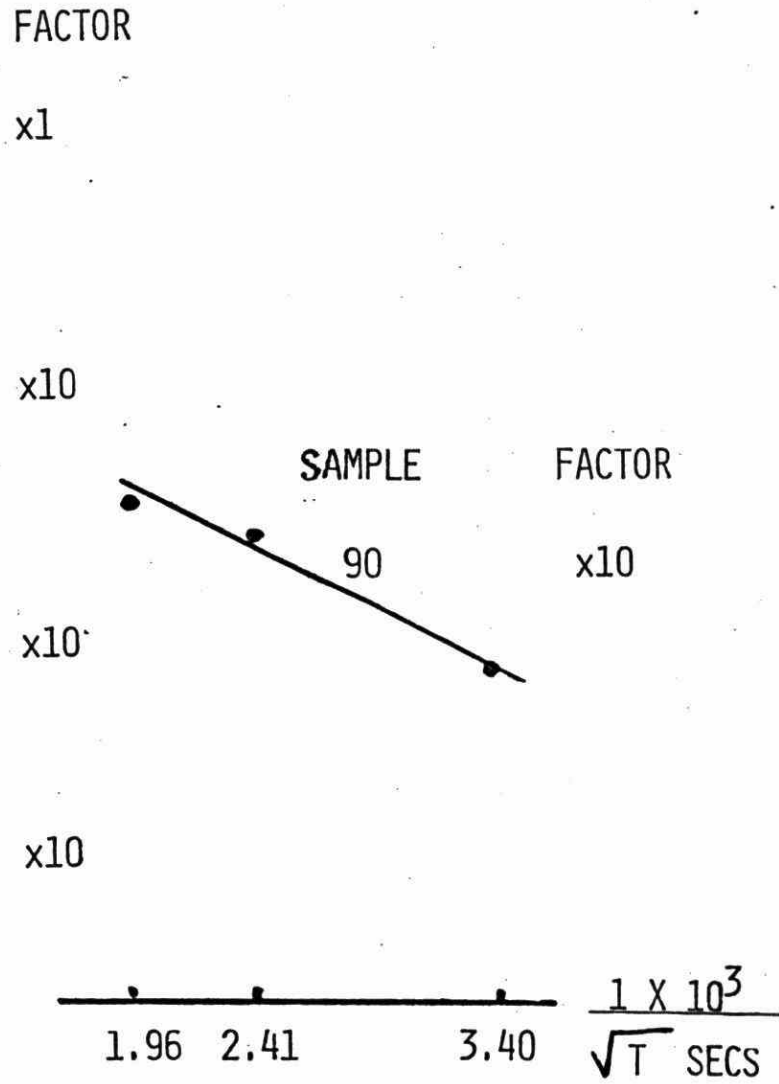


FIGURE XIII
VANADIUM



B10. MANGANESE, IRON AND ALUMINUM

MANGANESE

There was good agreement with the penetration theory (Figure XIV) for two samples of machinery manufacturing foundry sand and liquid waste residue (Nos 14, 15). However, the relationship did not appear to apply to another foundry sand (No 12) and a scrubber sludge (No 42).

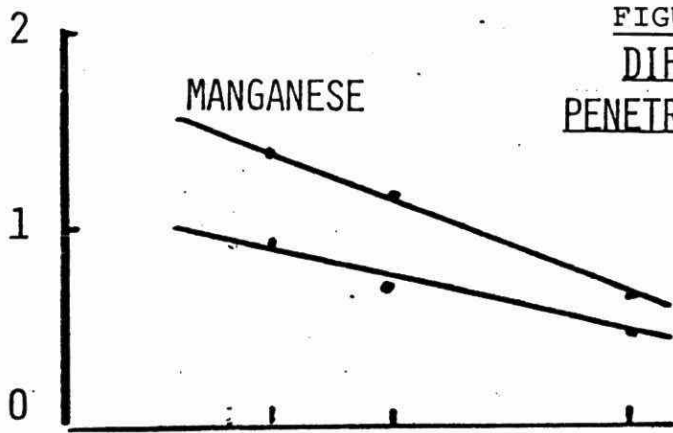
IRON

Leaching of some samples fitted the penetration theory (Figure XIV) for iron, such as a tailings sample (No 2), a topsoil sample (No 28), and lime-treated oil sludges (Nos 33, 34). There were some exceptions, such as steel wastes (Nos 39, 40), a plating waste settling pond (No 1), and an iron foundry sand (No 12).

ALUMINUM

Low concentrations of soluble aluminum were observed in a few leachates. A sample of foundry sand (No 14) and an associated liquid waste residue (No 15) conformed to the penetration theory (Figure XIV). In another foundry sand sample (No 12) the small amount of water soluble aluminum was essentially leached in the first cut.

FIGURE XIV
DIFFUSIVITY
PENETRATION THEORY

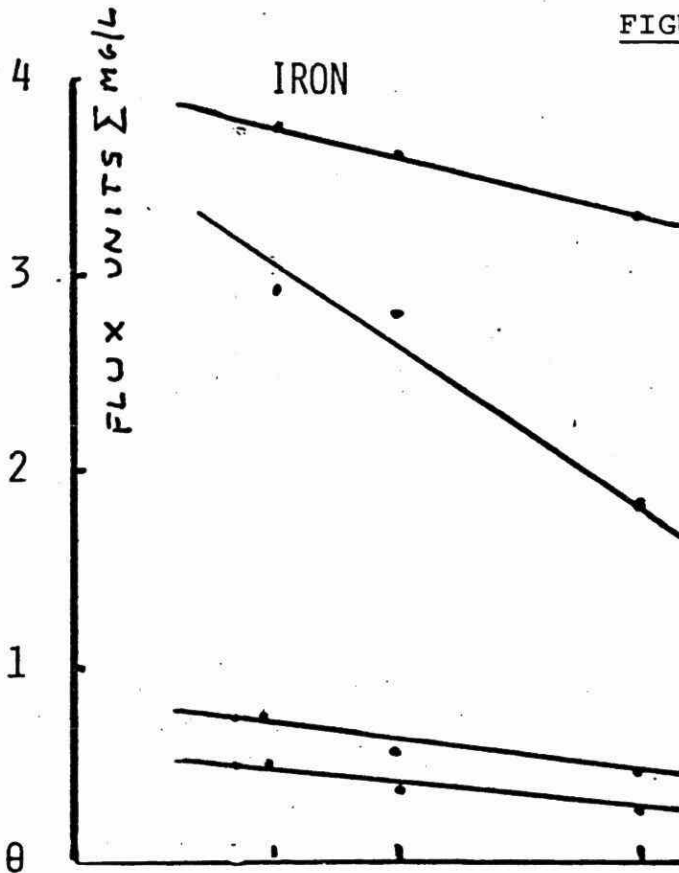


SAMPLE NO.

15

14

FIGURE XV

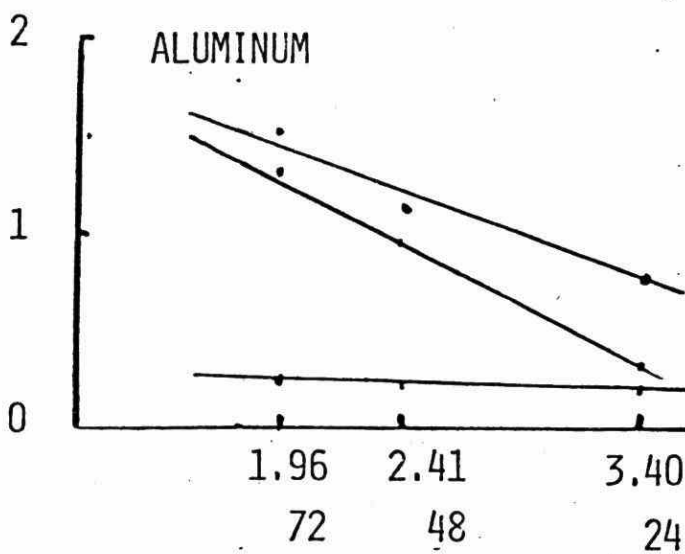


28

2A

33
34

FIGURE XVI



14

15

12

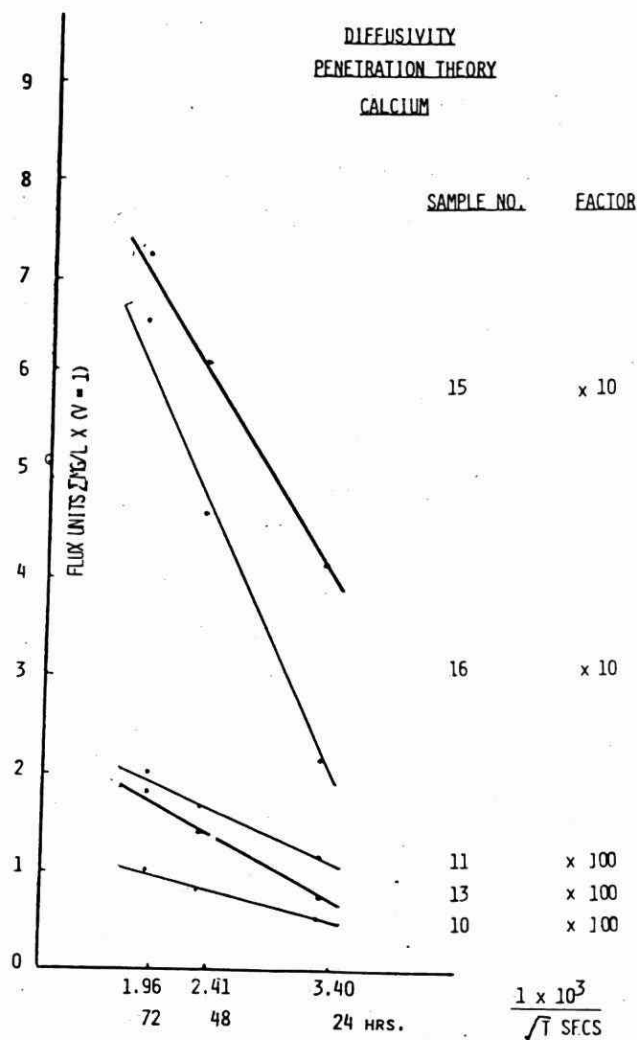
$\frac{1 \times 10^3}{\sqrt{t}} \text{ SEC.}$

B11. CALCIUM AND MAGNESIUM

CALCIUM

Calcium was readily leachable over a wide range of concentrations and for different types of waste. There was close agreement with the penetration theory for some samples (Figure XVII). In others, however, such as a steel manufacturing waste (No 85) and solidified wastes, the concentration of Ca increased in later cuts. This also occurred for Ba and Sr in No 85.

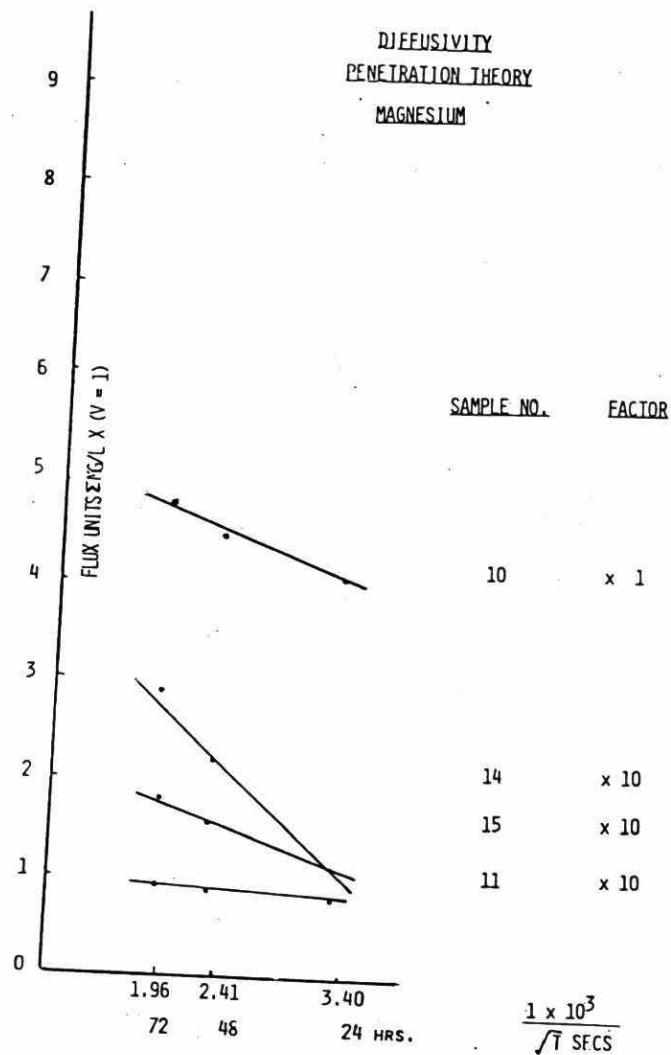
FIGURE XVII



B11. MAGNESIUM

Appreciable quantities of magnesium were leached from a few of the samples tested, such as a foundry sand (No 14) and other wastes. There was good fit with the penetration theory.

FIGURE XVIII

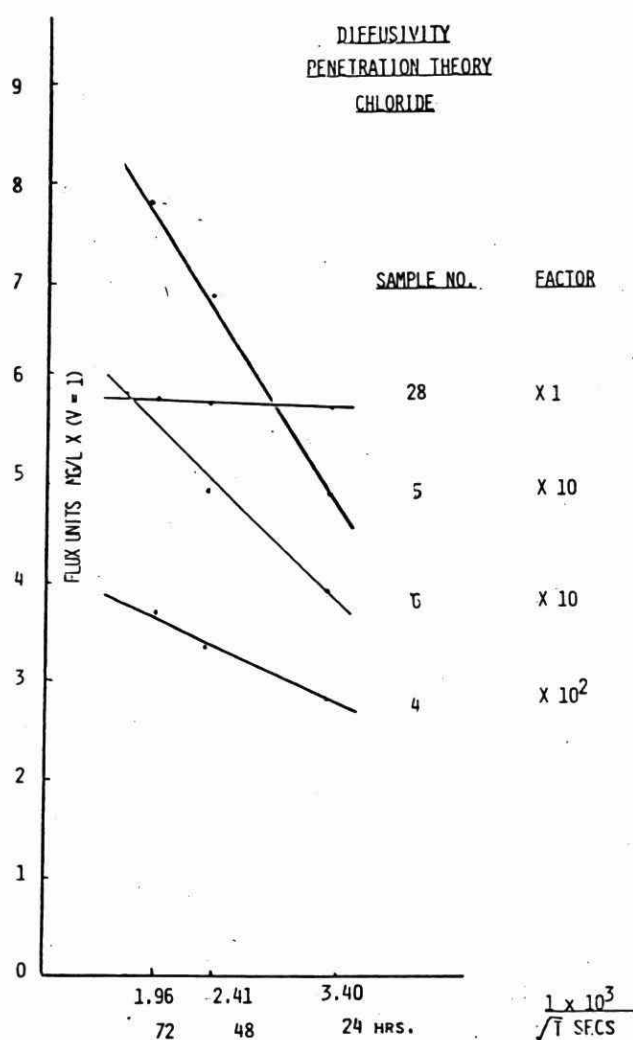


B12. CHLORIDE AND SULPHATE

CHLORIDE

Chloride was determined in three samples of fly and bottom ash (Nos. 4-6). There was good agreement with the penetration theory. In a sample of topsoil (No. 28), almost all the chloride was leached out in the first cut

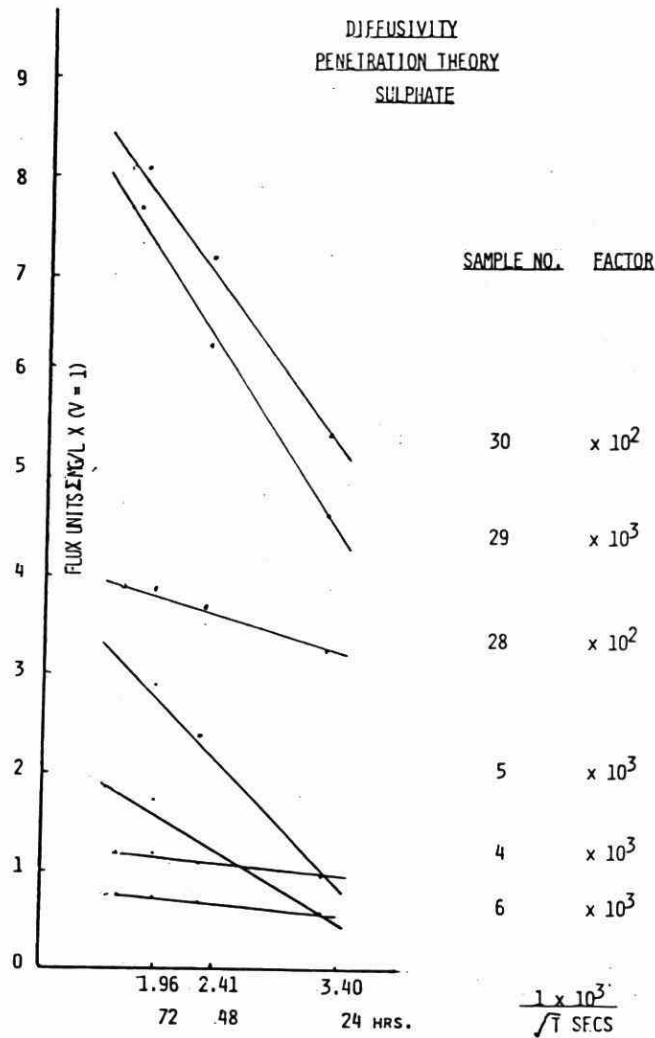
FIGURE XIX



B12. SULPHATE

Relatively high concentrations of sulphate were obtained in those samples tested: fly ash (Nos 4,5, 6), topsoil (Nos 28), and mine tailings (Nos 29, 30). In all cases there was good agreement with the penetration theory of diffusivity.

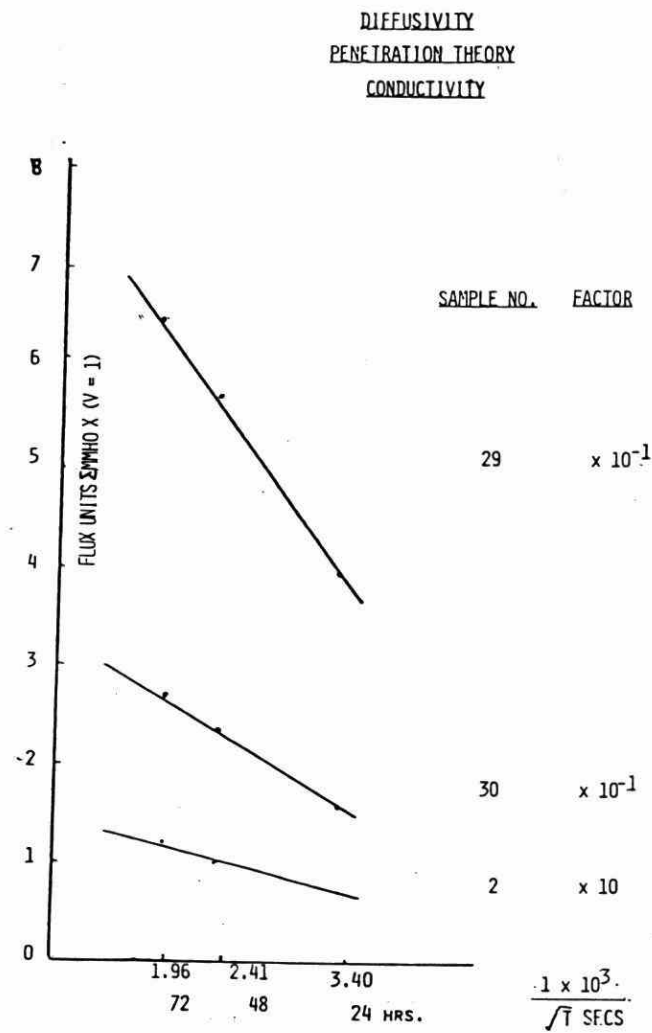
FIGURE XX



B13. CONDUCTIVITY

Excellent agreement with the penetration theory was obtained for conductivity (related to dissolved salts). A few examples are shown in Figure XXI.

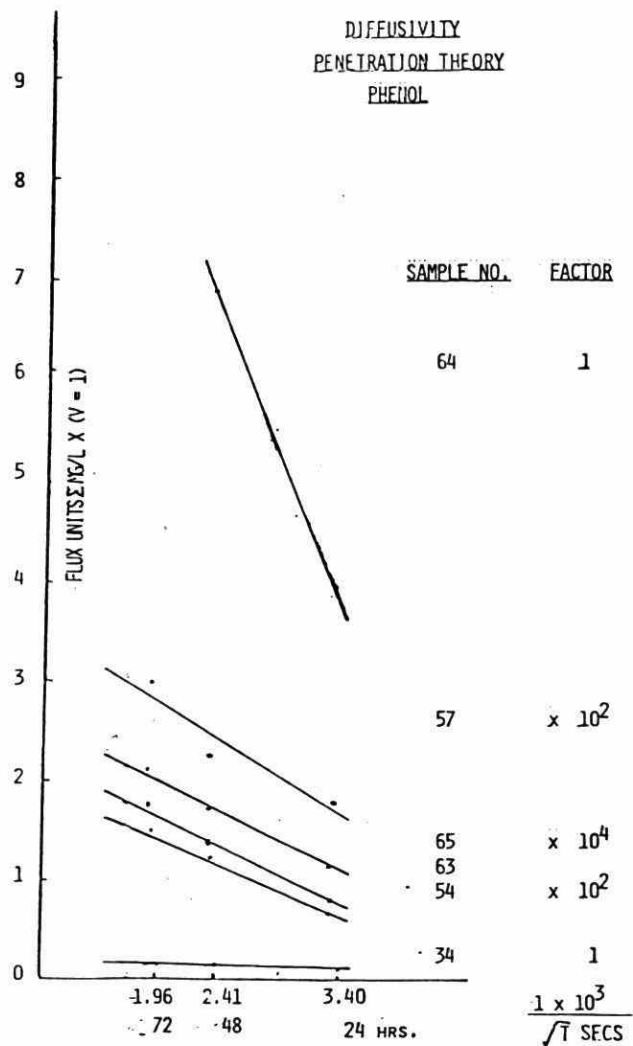
FIGURE XXI



B14. PHENOL

There was good agreement over a wide range of concentration of phenol in leachate from "fixed"/lime-treated oil sludges (Nos. 34, 54, 57), casting floor and scrubber settling tank (Nos. 64, 65) and a "cat cracker" (No. 63).

FIGURE XXII



B15. PHOSPHATE

Waste calcium hydrogen phosphate (CaHPO_4) was tested for leachability of phosphate (No. 91) with good conformity with the penetration theory for both soluble phosphorus and conductivity. As expected a very high concentration of phosphate was obtained in the first cut, decreasing rapidly with successive cuts. The pH of the first cut was unexpectedly low indicating the presence of free acid. Unfortunately, this was the only set analyzed for leachable phosphate.

TABLE VI

COLUMN LEACH TEST

CALCIUM HYDROGEN PHOSPHATE

SAMPLE No. 91

CUT	P mg/L	COND mmhos	pH
1	50,000	9,500	2.6
2	2,300	2,200	5.1
3	200	1,700	5.8

DISCUSSION

CONFORMITY WITH PENETRATION THEORY

It is speculated that the conditions of the "unsaturated" flow test, particularly the low flow rate, are conducive to movement by diffusion in and out of aggregates of particles, rather than surface run-off through the channels between particles. This could explain the agreement with the penetration theory of diffusivity in many instances.

It is evident from the plots that for parameters conforming to the penetration theory there is a wide range in effective diffusivities as judged by the variation in gradients of the linear plots. In some cases, however, such as for copper, gradients were very similar for many of the samples. Cadmium in bag-house dusts was of interest in that leaching conformed to the penetration theory at both very high and low concentrations.

In general, it appeared that conformity with the penetration theory of diffusivity was better for finely divided permeable samples, as is to be expected from the relatively large surface area to volume ratio.

Hot acid (HCl/HNO_3) extractable metal content was determined in some samples. It is evident, however, that for some metals such as iron there is little or no relationship with the quantity leached. For most metals, acidity as indicated by pH, was a more important factor. It is of interest to note that Mo (also Si) are exceptions in that significant quantities can be leached under basic conditions.

Particle size (surface area), mineral composition and degree of crystallinity are also important factors controlling rate of leaching.

It is more difficult to offer explanations for the exceptions to the penetration theory of diffusivity. It is suggested that for situations where almost all the parameter is leached in the first cut, the component could have either been present in the original liquid phase (and is displaced by the element) or was present in a relatively soluble form as a coating on individual aggregates.

Increases in concentration with time can be attributed to changes in common ion effects, pH, redox, removal of calcium, sulphide, etc. with progress of leaching, leading to dissolution. Surface area of aggregates could also increase during leaching resulting in a higher solution rate. Colloids may also tend to become mobile.

CHEMICAL FACTORS AFFECTING MOBILITY

During the leaching process in the unsaturated flow column test distilled water is contacted with the waste material and with the carbon dioxide of the air as it passes down the column. In the absence of other acids or bases acidity of the water will be dependant on the solubility of CO_2 in water as governed by Henry's Law, giving a calculated pH of 5.7. Acidity may be lower in the waste column if CO_2 is generated and diffuses at a slow rate out of aqueous solution. In practice, most waste materials are highly buffered, controlling the pH.

The environmental impact of ionic flux released from a waste as indicated by an unsaturated flow column leach test has to be viewed with respect to site specific factors discussed above and toxicity and chemical factors affecting mobility for each ion or contaminant. As discussed earlier the test is designed for aerobic (oxidizing) conditions; leaching rates can be expected to be different under reducing conditions.

Mobility of toxic cations is increased under acid conditions. Cadmium (II) and mercury (O,I,II) are retained less strongly by soils than the other toxic cations. Cadmium is extremely toxic (as well as being mobile and available to plants) and hence can be a serious problem at waste disposal sites. Mercury (II) is strongly held in soil but is easily reduced to the volatile $\text{Hg}(0)$. Some of the potentially toxic cations covered in this study are transition metals (Co, Ni, Cu and Zn). They normally tend to precipitate out as hydroxyoxides under aerobic conditions. Copper and zinc can, however, be strongly complexed by soil organic matter.

Attenuation of toxic metals through cation exchange and adsorption on soil minerals and organic matter also limit mobility.

Some of the elements discussed in this report form toxic anions, such as V, As and Cr. Their availability to plants (and mobility) decrease with Al and Fe hydroxyoxide content but increases slightly with pH. Chromium (VI) is of interest in that it moves as an anion (CrO_4^{2-}) through well aerated soils of moderate to high pH. Molybdenum is not considered toxic; indeed it is essential for symbiotic nitrogen fixing micro-organisms. It usually occurs as molybdate (HMoO_4^- and MoO_4^{2-}) which reacts strongly with Fe hydroxyoxides. Solubility and plant availability of molybdenum varies with pH.

The strong adsorption can be explained by ligand exchange in which the oxygen atoms on the hydrous oxide surface are replaced by weak anions such as arsenate, molybdate, phosphate and fluoride. The anions Cl^- , NO_3^- and SO_4^{2-} are non-specifically adsorbed to a minor degree on layer silicates and hydrous oxides under acid conditions. Their adsorption is negligible at $\text{pH} > 7$.

The retention of non-ionic organic compounds such as phenol is also of interest. Several mechanisms can be involved, such as molecular characteristics, acidity or basicity, water solubility, polarity, size and polarizability (Bohn et al, 1979).

Manganese, iron and aluminum occur in soils in high concentrations and, except for Al at low pH, are not toxic. They are important, because of their relative abundance, in relation to toxic ions in that they precipitate out as hydroxyoxides with varying degrees of hydration, e.g. $\text{Al}(\text{OH})_3$, AlOOH , Al_2O_3 , FeOOH , Fe_2O_3 and MnO_x . They also act as buffers, combining with both H^+ and $(\text{OH})^-$. Ion activities, except for Fe(III) are usually much lower than those calculated from solubility products.

The toxic Al^{3+} ion is predominant below pH 4.7, with $\text{Al}(\text{OH})_2^+$ and then $\text{Al}(\text{OH})_3$ forming at higher pH's, with $\text{Al}(\text{OH})_4^-$ above pH 8.

Solid phase $\text{Al}(\text{OH})_3$ can precipitate out over the entire range of pH when its solubility product is exceeded.

Retention of the hydroxyoxides in soils is even higher than that suggested by hydroxyoxide formation, due to mechanisms such as co-precipitation, adsorption and organic complexation. Iron (III) may be an exception in that with aeration $\text{Fe}(\text{III})$ concentrations agree with those calculated from the solubility product of FeOOH (Bohn et al, 1979).

Trace metals may be present as contaminants in amorphous gels of the hydroxyoxides and hence their solubility would be controlled by the dissolution rate of the major component. Availability of toxic anions such as Se, V, As and Cr decreases with Al and Fe hydroxyoxide content, as discussed earlier. Iron in some forms, such as steel-manufacturing waste, can be highly insoluble, probably because of its exposure to high temperature under oxidizing conditions.

Development of reducing conditions can have a marked effect, such as through the reduction of $\text{Fe}(\text{III})$ to the more mobile $\text{Fe}(\text{II})$ and MnO_x to $\text{Mn}(\text{II})$. Sulphide and carbonate precipitation occur rather than the hydroxyoxide.

The presence of Ca and Mg play a significant role in leaching, particularly if present as carbonates. They tend to preserve basic conditions, thereby precipitating out hydroxyoxides (and carbonates) of heavy metal cations. In a soil system, the calculated pH for the equilibrium between free CaCO_3 and the normal CO_2 content of the air (0.03%) is approximately 8.2. At this pH soil hydroxy-Al compounds are essentially neutralized, as discussed earlier. Under the conditions of the unsaturated flow test it can be assumed that equilibrium of the water with atmospheric CO_2 is attained.

Calcium and magnesium tend to leach at a relatively rapid rate when present as the carbonates. When carbonates are in excess of several per cent they control pH and Ca^{2+} in solution. The presence of Ca and Mg in leachate is desirable in that they tend to reduce the toxic effects of the heavy metals.

Measurement of alkalinity and buffering capacity of a waste by titrating with acid and plotting pH against milli-equivalents of acid is a useful tool for assessing the capability of a waste for withstanding attack by acids. Additional information can be gained by analyzing aliquots withdrawn during the titration for metals of interest; as discussed earlier for solidified steel-manufacturing waste (Section A6).

TEST LIMITATIONS

The unsaturated flow column test is intended to simulate the action of rain-water infiltrating through a permeable waste at a low velocity. The system can be compared hydrodynamically with infiltration of rain water in unsaturated soil. Haverkamp and Vauclin (1981) found that the Kirchoff transformation provided a better fit between experimental and theoretically determined values than the Richard equation. This was considered to be important with respect to coupled transfer problems, such as water and pollutants. Upward transport by evaporation, which can also be significant, also follows the Kirchoff transformation.

The test provides some indication of pollutant mobilization in a waste under aerobic conditions. Leachate/ground-water interaction, however, is site specific and is dependent on leachate quantity and composition, the ground-water system (composition and flow pattern) and physical and chemical properties of the sub-surface soil and rocks. Mathematical models have been derived to relate the various parameters involved in mass transport processes of simultaneous diffusion, convection and chemical reaction (Fungaroli and Steiner, 1979).

Factors such as evaporation, dilution, attenuation, chemical and biological decomposition processes, and the possibility or otherwise of channelling must be considered in relation to transport of pollutants and toxicity effects.

Results of column leach tests with distilled water under unsaturated flow conditions must, therefore, be considered in relation to the various factors affecting transport of pollutants at each disposal site. If the waste material is likely to be exposed to conditions other than percolating rain water, e.g. could be submerged below the water-table or contacted by leachate from other wastes, other test conditions should be used.

In some instances, the waste was relatively impervious from the start of the test or became so as the test progressed, resulting in a reduced rate (or no flow) under saturated condition, e.g. some plating wastes.

Processes other than the penetration theory of diffusivity are likely to be operative. Reducing conditions, initially present or developing during the test, will have a major effect.

The test in its present form is not suitable for testing the leaching of contaminants such as PCB's because of the use of plastic equipment and the introduction of uncontrolled high blanks. Glass equipment is required for such tests.

It is not always feasible to test for all possible contaminants with present analytical support in which some parameters have to be measured individually. Unsuspected contaminants can be missed and associated ions which are important with respect to toxicity, e.g. Ca and Mg, may not be analyzed. This situation can be expected to improve with the application of simultaneous multi-element analysis, such as by direct reading emission spectrometry, powder spectrograph, or X-ray fluorescence analysis of the solids after evaporating leachate to dryness. The ion chromatograph could also play a useful role for determining several anions in one test.

Some of the limitations of the present test and other procedures were reviewed earlier by the author (Darcel, 1981). Some suggestions were offered for method development and evaluation. An additional consideration is that the flow rate of 300ml/24hours was arbitrarily selected for convenience to permit a relatively rapid test. The flow rate (equivalent to 31 cm, or 12 in. water every 24 hours) is much higher than the fraction of rain water expected to infiltrate on an annual basis.

It is suggested that modifications to the test would improve the closeness of fit with the penetration theory in some instances. These changes could include the prior removal of free liquid from the sample to be tested or, if dry, pre-wetting it to its moisture holding capacity, preferably by capillarity. The first leachate cut will then be of the same volume as successive cuts. Analysis of leachate after 4 to 6 hours in addition to the first 24 hours for each parameter could also provide an additional data point for testing linearity of the relationship with time for the penetration theory.

Unfortunately, no data was obtained for silica or fluoride. Many of the leachates were basic, conducive to the leaching of silica and its complexes. Measurement of fluoride could also have been useful in some instances, because of the formation of complexes between fluoride and metals such as aluminum and lead.

Chemical and physical processes other than diffusion can also be operative. Salts brought into solution by the percolating water can precipitate lower in the column due to chemical changes, e.g. degree of saturation, pH, redox or carbonation by carbon dioxide in the air or reaction with carbonates. Precipitates initially in suspension can be filtered out and/or absorbed on the particles of waste as the liquid passes down the column.

Concepts such as the saturation index (Troup, 1974, Matisoff et al, 1980), and the related parameters of ion activity product and solubility constant for the minerals of interest in a sample are important with respect to free energy requirements for precipitation or solution (Bohn et al, 1974; Matisoff et al, 1980). It could, therefore, be interesting to know the mineral form of toxic metals, e.g. the carbonates, phosphates and sulphides of zinc, cadmium and lead. It is unfortunate that measurements of these anions and mineral composition are lacking in the present study.

CONCLUSIONS:

1. The column leach test in its present form is a relatively simple test requiring a minimum demand on technician time or expertise (other than for the analysis of leachates).
2. The leaching of many ions with distilled water conforms with the penetration theory of diffusivity in many instances in the M.O.E. unsaturated flow column test.
3. The test in its standardized form is useful in assessing relative rates of mobilization of pollutants.
4. Some finely divided waste, such as bag-house dusts, are most susceptible to leaching toxic metals.
5. The use of 24, 48, 72 hour leaches is practicable and adequate for samples conforming to the penetration theory of diffusivity.

RECOMMENDATIONS:

1. Results for laboratory column leach tests should be used in conjunction with site-specific factors in assessing the potential hazards of pollutant mobilization.
2. Consideration should be given to removing free liquid from the sample prior to the leach test to permit more consistent conformity with the penetration theory of diffusivity. Results should be tested for conformity with this theory and non-conforming data checked and explanations sought.
3. The practice of using a minimum of three 24 hours cuts should be continued (to allow testing the theory of diffusivity). In some instances, the range should be extended, e.g. to cover 4-6 hours and 96 hours.
4. More effort should be directed towards determining the relatively insoluble mineral species, by quantitative measurement of carbonate, sulphide, phosphate and silicate anions, mineral compositions, and degree of crystallinity. Particle size distribution should be determined especially for fine grained materials.
5. The present practice of using the column leach test as one option for testing a waste should be continued. In some instances, depending on the form of the waste, shake or static testing with water or acid may be preferable. Determination of alkalinity would also be advisable for some wastes.
6. Suggestions for method development made in the earlier report (Darcel, 1981) should be implemented.
7. Effort should be directed at employing simultaneous multi-elemental techniques to the analysis of leachate and the original waste such as direct reading emission spectrometry, emission spectrograph(plate), or X-ray fluorescence.

Application of these procedures would provide faster, cheaper and more comprehensive assessment of the potential for leachate production from the inorganic components in a solid waste.

8. Leachate should be tested for dissolved organic carbon (DOC) and, if the presence of specific organic contaminants is suspected, the determination of their concentrations in the leachate and/or the original waste.
9. Measurements should be made of the 5-day Biological Oxygen Demand (BOD_5), particularly with respect to the effect of dilution or interferences, as an indicator of toxicity. Chemical Oxygen Demand (COD) should also be determined to obtain an assessment of non-biodegradability.
10. Rapid toxicity tests should be conducted under standardized conditions through the use of a Beckman Micro-Tox (already evaluated by the M.O.E. Microbiology Section), with back-up by *Daphnia*, *Bacillus coli* or *Pseudomonas fluorescence* toxicity tests.
11. Certain analytical tests on leachate should be mandatory; for example, pH, conductivity, DOC and (if/when available) the Micro-Tox toxicity test. If the values obtained in these preliminary tests indicate a potential problems, other tests should then be mandatory, such as a metal scan by emission spectrometry or analysis for specific toxic organic compounds.

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APPENDIX I

TEST MATERIALS

<u>Sample No.</u>	<u>Laboratory No.</u>	<u>Description</u>
-1	S7-28.29	Settling pond
2*	S7-31.129	Silver Smelter
3	S8-33.48	Buffing compound
4	S8-41.6	"Old" fly ash
5	S8-.7	"New" fly ash
6	.8	Bottom ash
7	S8-47.5	Primary sludge
8	S8-49.3	Mine Tailings
9	S9-10.1	Carbon
10, 11	S9-22.1, 2	Waste
12	S9-37.1	Iron foundry sand
13	S9-64.1	Filtered plating sludge
14	S9-69.1	Foundry sand
15	.2	Liquid waste residue
16	S9-76.1	Waste -
17	S9-95.1	Sludge
18	S9-104.1	Fill
19, 20	S9-139.1, 2	Surface soil
21-24.	S9-162.1-4	Paper waste
25	S9-199.12	Bag house dust
26	S9-222.1	Ditch
27	S9-223.1	Metal casting
28	S9-240.1	Topsoil
29	S9-264.1	Gray Tailings
30	.2	Yellow Tailings
31	SO-66.1	Dewatered sludge
32-34.	SO-72.1-3	Lime - Treated sludge
35-38	SO-80.1-4	Sub-division development
39-40	SO-82.1-2	Steel waste
41	SO.93-1	Filter cake
42	SO-108.1	Scrubber sludge
43, 44	SO-159.1-2	Bag house dust
45, 46	SO-202.1-2	Insulation
47-50	SO-203.1-4	Solidified waste
51, 52	SO-214.1-2	Fixed sludge
53	SO-215.1	Bag house dust
54, 55	SO-217.1	Fixed sludge
56, 57	SO-240.1-2	Fixed sludge
58	SO-265.1	Solidified waste
59	SO-269.1	Foundry sand
60	SO-273.1	Foundry sand - core
61	.2	- cupola bottom
62	SO-275.1	Catalyst
63	SO-286.1	Cat cracker
64	SO-309.1	Casting Floors
65	.2	Scrubber settling tank
66-68	SO-324.1-3	Steel making waste
69	SO-328.1	Metal Sludge

*2A S7-37:13-27

Arsenic wastes

APPENDIX I

TEST MATERIALS

<u>Sample No.</u>	<u>Laboratory No.</u>	<u>Description</u>
70	Sl-26.1	Foundry sand
71-75	Sl-34.1-5	Waste
76	Sl-35.1	Oil treatment
77-81	Sl-52.1-5	Lime waste
82-84	Sl-54.1-3	Brass smelter
85	SE15-9001	Bag-house dust
86	Sl-67-1	Bag-house dust
87-89	Sl-44.1	Solidified steel waste
90	SE17-9007	Spent catalyst
91	Sl-63.1	Calcium phosphate

Method A

LEACHING POTENTIAL
COLUMN LEACH TEST - METHOD A1. Introduction

Laboratory leach tests on minimally disturbed samples using unsaturated flow are used to predict the leaching potential of industrial wastes expected to remain above ground water level. Distilled water is usually used as leach where the waste is expected to be contacted only by rain water. Other leaching solutions may be used to test for other disposal situations, such as in landfill sites, e.g. N ammonium acetate, pH 4.8, ground water collected from the area, or carbonated water. The material is then leached under unsaturated flow conditions.

Leach liquor is delivered from a reservoir at a controlled rate usually below the permeability rate for the material.

The method should be considered tentative pending resolution of the optimum procedure, preferably through the ASTM.

The method more closely simulates field conditions than shake tests, such as those prepared for adoption by ASTM. However, it is less realistic than the simulated Field Leaching Test which may be more suitable for some samples. If the material is expected to be under water, the saturated flow procedure - Method B should be used.

2. Interferences and Shortcomings

It is not possible to exactly simulate field leaching conditions in the laboratory. Laboratory leaching tests of necessity have to be relatively short term whereas it is desirable to determine the effect of many years leaching. Disturbance of the material cannot be avoided in laboratory testing and it is not practicable to use a column length similar to the depth of material in the field. The chemical composition of rain or other leaching media and its variable and intermittent flow rate also cannot be duplicated in the laboratory. However, by standardizing leaching conditions for a set of samples an estimate can be obtained of relative rates of leaching.

Determination of
Leaching Potential

Ministry of the Environment
July 26, 1978

Method A

Permeability of the material may be lower than the percolation rate of the leach liquor resulting in a build-up of leach liquor above the surface and the development of saturated conditions. The test would then be conducted similar to Method B (Saturated Flow). Alternatively, for some applications, the test will have to be modified to increase the permeability, such as by the incorporation of a filter aid such as Celite.

The test as such does not evaluate the effect of alternate wetting and drying with possible migration upwards during dry periods and hence reduction in net leachate flow.

No account is taken of potential surface run-off. A more elaborate procedure is required such as the Simulated Field Leaching Test - Method C.

Since the method is intended to attempt to simulate natural conditions, for some types of heterogeneous wastes with large hard particles, wider diameter cylinders may have to be used.

3. Apparatus

- a) Reservoir and column as per Figure 1. Drop flow rate controlled by length of Technicon flow tube (approximately 0.5cm long) - 0.005 in I.D. - Technicon 1160532 - 01; Esbe AB-29-1321.
- b) Collection bottles - sample bottles - approx. 1 litre.
- c) Stop watch or timer.
- d) Balance top loading - to 1000 g.
- e) Graduated cylinder, 10 ml.
- f) Glass wool.

4. Reagents

- a) Leach liquor - as specified for test (normally distilled water).
- b) Preservatives for metals, phenol, etc. as specified for test.

Method A

5. Procedure

- a) Set up reservoir and column as shown in Figure I.
- b) Tamp down glass wool plug at base of column.
- c) Use minimum glass wool to minimize hold up of leachate. Check flow rate from reservoir using timer or stop watch and 10 ml graduate. Replace or adjust length of flow tube as required.
- d) Check spacer will position flow tube in centre of column. Weigh out 100 g air-dry waste after breaking up lumps greater than about 1 cm. Transfer to column with minimal disturbance.
- e) Place clean sample bottle below column. Add preservative, if required.
- f) Place 300 ml leach solution in the reservoir and commence test.
- g) Continue leaching until first "cut" of 300 ml collected (or less depending on amount absorbed by column).
- h) Discontinue test if 24 hour leach specified; alternately, collect a second 24 hr. "cut".
- i) Note volume, turbidity, colour, pH and conductivity, of the leachate. Divide into aliquots and add preservative(s) as required for tests on leachate.
- j) Determine moisture content of material leached if results are to be expressed on an oven-dry weight.
- k) Determine "total" or "extractable" content of pollutant of interest on separate sub-sample.
- l) Repeat leach procedure with other leach media if required.
- m) Analyze leach liquor for "blank".

*Determination of
Leaching Potential*

*Ministry of the Environment
July 26, 1978*

Method A

6. Calculation and Reporting

Results for each parameter are normally reported as mg/l in each leachate cut and in ug/g oven or air-dry weight of material (except pH and conductivity).

$$\text{ug/g} = \frac{\text{mg/l} \times \text{volume of cut in mls}}{\text{dry weight of sample in grams}}$$

Leach liquor blanks are normally negligible and are ignored.

Results are reported to two significant figures.

Material leached can also be expressed as percentage of "total" or "extractable".

Total = ug/g x number of grams in column.

7. Precision and Accuracy.

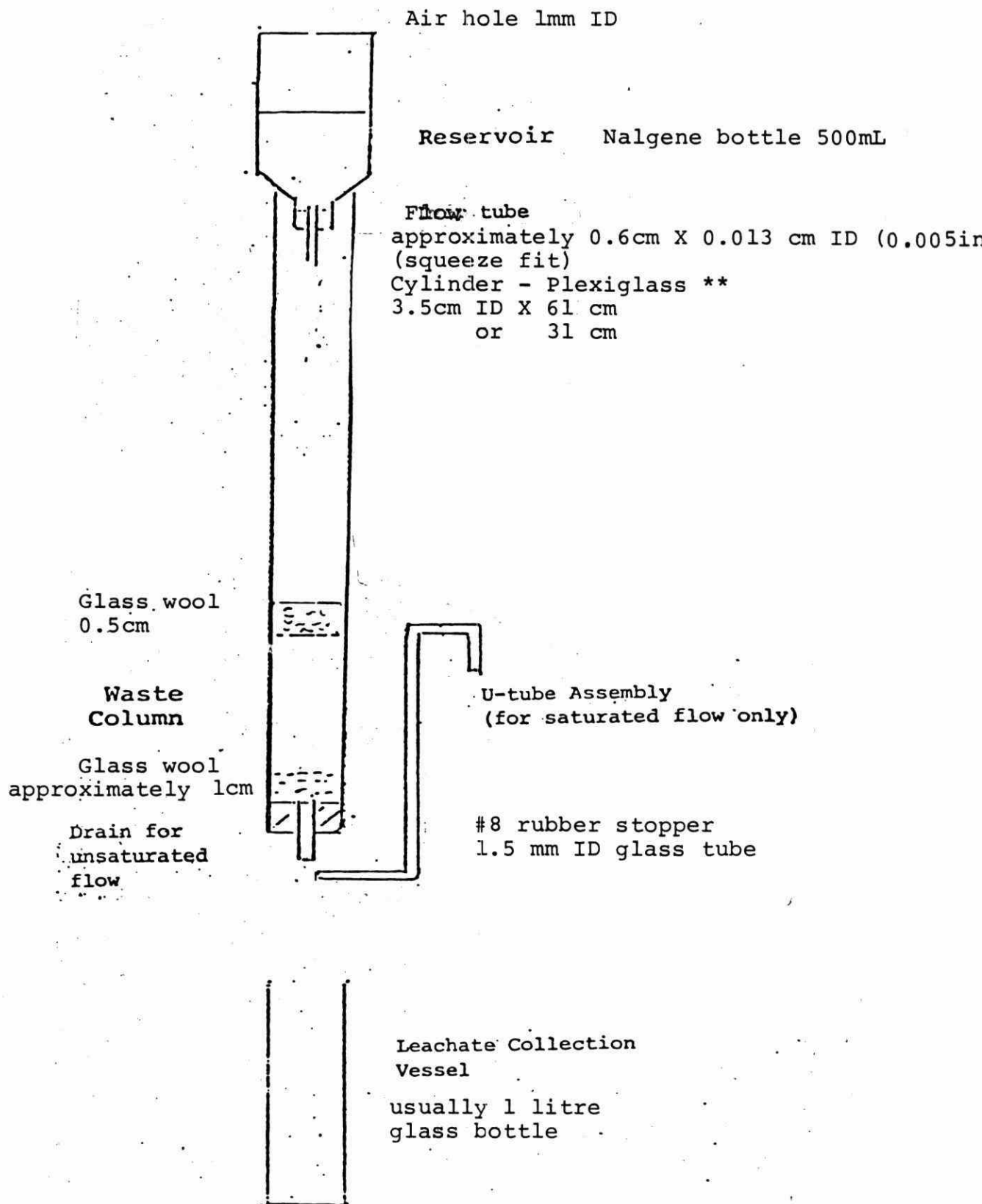
Not determined.

8. Bibliography

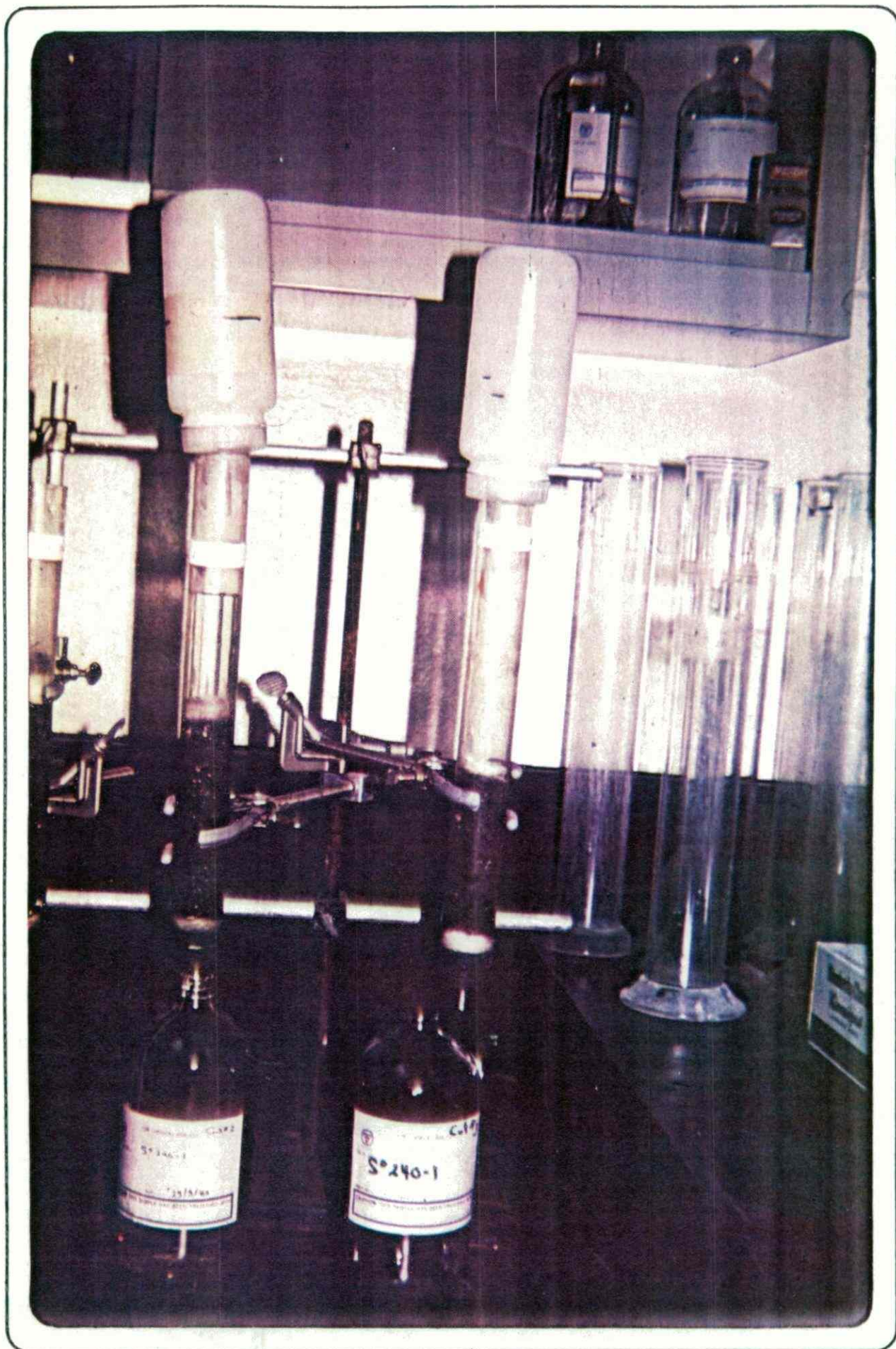
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FIGURE I

OMOE LEACH COLUMN



** obtainable from Miller Plastics, Toronto, Ontario



LEACHING ASSEMBLY

APPENDIX III
REPRODUCIBILITY

No. 83 Steel-manufacturing waste

	Run No	Mo Mg/L	Cu Mg/L	Cond mmhos	pH	Vol ml
Cut 1	1	10.3	.10	15000	9.1	210
	2	9.4	.10	14000	9.4	220
	3	10.2	.10	14000	9.1	230
Cut 2	1	7.3	.02	2000	9.1	300
	2	7.6	.02	1900	8.7	300
	3	7.6	.06	2150	8.7	300
Cut 3	1	5.6	.02	1800	9.3	300
	2	6.2	.02	1800	9.0	300
	3	5.4	.02	1750	8.9	300

Zn, Ni, Pb and Cd below detection limits for A.A.S. of
.02, .06, .06 and .008 mg/L respectively in all cuts.

1D
380
057
1981b